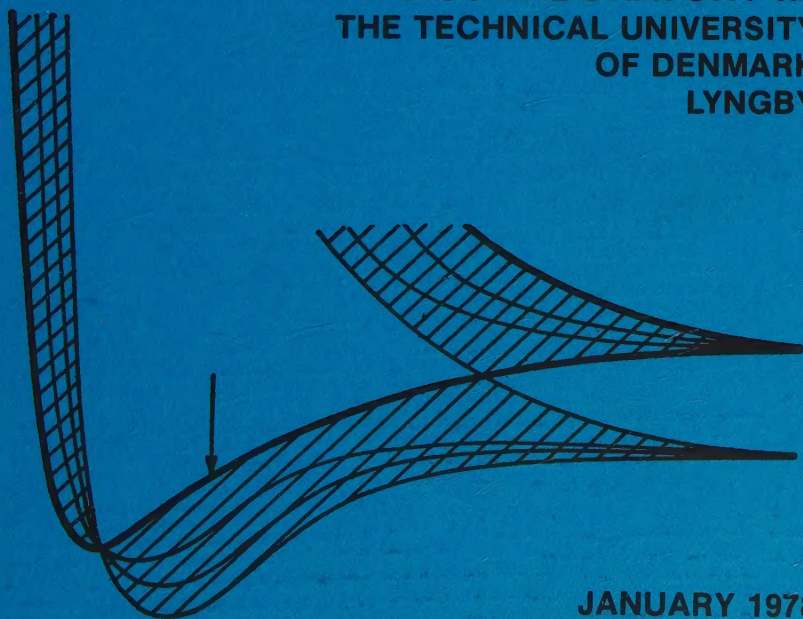


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THE INFLUENCE OF HOLES ON THE PHONON SPECTRUM OF SEMICONDUCTORS

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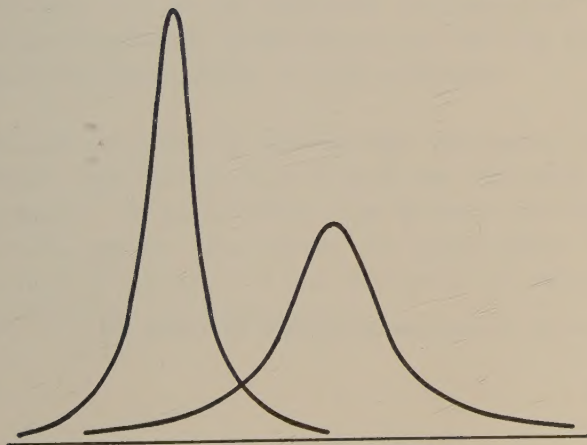


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Peter Lawætz
Physics Laboratory III
The Technical University of Denmark
1978



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Carl Th. Pedersen
h.a.dec.

PREFACE

The present work deals with semiconductor theory. I have been fascinated by this field for nearly 15 years due to the variety of phenomena occurring in these materials, the large amount of detailed knowledge accumulated, and the very close connection between fundamental research and technical applications. Said in a few words, theory has worked extremely well in this area.

My own activities in the field have mostly been concerned with the properties of missing electrons which for all purposes can be treated as positively charged particles - the so-called holes. Although holes are conceptually simple, their basic features are rather complicated even in ordinary semiconductors. Consequently, much pertinent theory involving holes is hampered by approximations, and extraction of useful quantitative information is often not possible. The present work emphasises quantitative detail whenever reasonable, and I hope to have shown that within the subject treated there is no need to accept approximations otherwise necessitated by the complicated properties of holes.

On the other hand, too much detail may easily distort the presentation of the physical picture, and so I have chosen to leave out documentation on many of the secondary problems which actually consumed most of the time spent on the total project.

I am indebted to Professor Niels Meyer and the staff of Physics Laboratory III at the Technical University of Denmark for their continued interest in my activities and for providing a critical scientific environment of high standard.

I should also like to acknowledge the useful exchange of ideas, methods, and results that I have had with many colleagues around the world. In particular, I am grateful to Darrell Sell of Bell Laboratories who contributed the experimental background for the analysis in Section 5.2 and initiated my interest in dealing properly with nonparabolicity.

Thanks are due to Lis K. Hansen, Else Winther, and especially Margot Frederiksen for typing the manuscript, and to Birgit Olsen for drafting the figures.

Statens Naturvidenskabelige Forskningsråd has supported the publication.

Let me finally express my appreciation of all the people who by their interest convinced me that aspiring for the doctor's degree is worth while. My father was one of them.

Lyngby, June 1977.

Peter Lawatz

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1. INTRODUCTION

When two independent modes of vibration of a system are weakly coupled, the resonance frequency of anyone excited of the modes is slightly changed, and the mode is damped so that the resonance spectrum is broadened. In semiconductors, there are two fundamental types of modes: Particle excitations related to the electronic system, and phonon excitations in the lattice system of dressed nuclei. In this work, we study some specific situations where the coupling of the above subsystems leads to observable shifts and broadenings of the excitation spectra. We are then able to extract quantitative information on the coupling strength from analyses of existing experimental data. This knowledge should be relevant for other situations like transport phenomena where the electron-phonon coupling is of primary importance.

The electronic system of a pure semiconductor is well represented by the independent-particle model, where the one-electron band states are populated by electrons according to the Fermi distribution. In the ground state, there is an energy gap between the filled valence bands and the empty conduction bands. Changes in this state are produced by thermal and optical excitations of electron-hole pairs (where an electron is excited to the conduction band leaving a hole behind in the valence band) and by doping with impurities (which either donate additional electrons to the conduction band or accept electrons from the valence band again leaving free holes). Doping, which will be of particular interest in the present work, will not only add new particles to the system. It will also to some extent change the particle energy spectrum, but we shall leave this point to a later discussion.

Phonons are the quanta of vibrations in the lattice. The zero-point vibrations are always present, and additional excitations can be produced thermally, by optical methods like Raman-scattering, and by interaction with particles such as electrons, holes, and neutrons. Doping with substitutional

impurities will not add new excitations to the lattice system, but may modify the lattice spectrum. We shall return to this problem at a relevant stage.

The shifts and broadenings observed in the spectrum of one subsystem will depend on the state of the remaining system. For example, the electronic spectrum depends on temperature through the thermal population of phonon states, and the phonon spectrum depends on the number of free carriers as controlled by doping. Of course, not all situations are favorable for observation and interpretation, but the freedom provided by the general nature of the effects and by the present state of the art of semiconductor technology offers many possibilities which have not been fully exploited before.

As the title indicates, this work will mainly deal with the influence on the phonon spectrum of various hole concentrations produced by doping. An illustrative part of the phonon spectrum of pure Si is shown in Fig. 1.1.

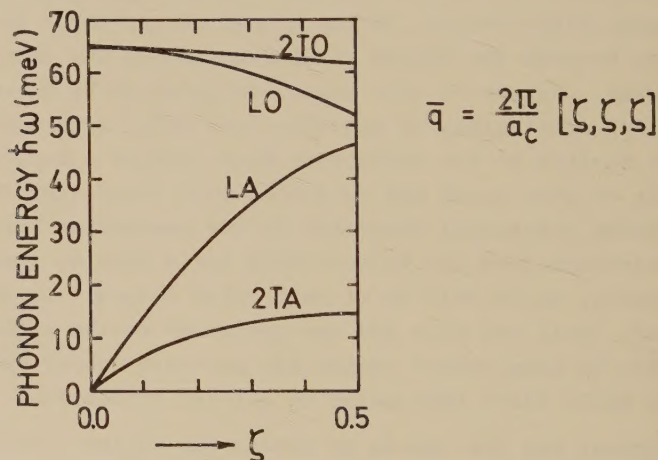


Figure 1.1. Phonon energy spectrum $\hbar\omega(\bar{q})$ of pure Si for wave vectors $\bar{q} \parallel \langle 111 \rangle$ (Dolling 1963). The long-wavelength region is at the extreme left of the diagram. a_c is the cube-edge lattice constant.

Two regions will be of particular interest: The long-wavelength acoustic and optic areas. Of these, the optic phonons can be probed by Raman-scattering, and the acoustic phonons or rather the ultrasonic portion is also directly accessible with accurate measurements. As discussed later, neutron scattering could indeed be used throughout most of the Brillouin zone, but information regarding the hole-phonon coupling in the long-wavelength region is most relevant for use in other contexts, and the effects to be studied are expected to be particularly large there.

The coupling between long-wavelength phonons and electrons or holes is described by means of the deformation-potential concept originally proposed by Bardeen and Shockley (1950): A long-wavelength lattice vibration may be regarded as a spatially varying, but locally homogeneous strain of the crystal, so that the perturbing Hamiltonian is the same for lattice scattering as for homogeneous strain, and thus the matrix elements of the coupling can be expressed in terms of the few parameters determining the change in band structure due to strain.

It would thus appear that the coupling parameters could be determined completely by studying the electronic spectra of statically, homogeneously strained crystals. However, this is not entirely true.

For instance, the homogeneous deformation associated with a long-wavelength optic phonon cannot be produced statically. Similar difficulties are encountered for asymmetric strains, but these are of limited interest anyway (Lawaetz 1969). We should also point out that the deformation-potential concept does not give the complete picture of the coupling (Lawaetz 1969): Long-range interactions of multipole character give non-analytic behavior at long wavelengths and act differently under homogeneous and nonhomogeneous conditions. It follows that there is a clear need for supplementary investigations involving dynamic experiments.

Even in some cases where the deformation-potential idea is applicable, the present methods may yield more accurate

coupling parameters than static-strain experiments.

The main purpose of the present work is the determination of coupling parameters for holes and long-wavelength phonons by detailed interpretation of shifts and broadenings in the spectra. In the treatment we distinguish between the phonon effects on the electronic spectra and the hole effects on the phonon spectra, with particular emphasis on the latter. This division is mainly for practical reasons, and it is shown that these apparently reciprocal effects are formally identical. Another distinction to be made is that between adiabatic and isothermal excitations, i.e., whether the observed spectrum reflects changes in internal energy or free energy. When we study the acoustic spectrum by measuring the sound velocity or elastic constants, the lattice motion is so slow that the background hole distribution is in thermal equilibrium with the instantaneous ionic positions or nearly so. It is then a free-energy problem. On the other hand, the oscillation of an optic phonon is so fast that the hole distribution does not relax during an oscillation, so it is a question of internal energy. A similar difference exists between the free-energy gap appearing in the thermal intrinsic carrier concentration and the electronic energy gap as observed in interband optical transitions. Although the two sides will be approached by different formalisms, it turns out that the results are formally almost the same.

As indicated in Fig. 1.1., the long-wavelength part of the phonon spectrum is relatively simple, but this is not so for the hole energy spectrum. Chapter 2 is therefore devoted to the hole spectrum of elemental and related semiconductors. The valence-band edge of the pure materials is complicated by degeneracy and spin-orbit splitting, and the hole-energy bands are nonparabolic. These features are responsible for large effects, and an exact treatment, notably of the hole phonon coupling matrix elements, is necessary in order to achieve quantitative reliability of the theoretical results to be compared with experimental data. The analytical derivation of the matrix elements may be the most important

detail of the present work. The results turned out to be crucial for quantitative success, and they may be used in many other contexts.

To obtain observable effects, large hole concentrations are needed. However, the doping impurities producing these holes will also affect the energy spectrum as dealt with qualitatively at some length in this chapter. A brief discussion of the possible direct effects of doping on the phonon spectrum is included to make sure that such features need not concern us further.

The real story begins in chapter 3 with the effect of holes on the elastic constants, that is, the acoustic phonon region. An extensive collection of experimental data exists, but the earlier attempts to extract the acoustic deformation potentials b and d were rather discouraging because the derived values were almost without exception much larger than found in static-strain experiments with optical spectra. The present theory including an accurate treatment of the hole-energy bands yields very promising results. Starting with a general free-energy model (Bir and Tursunov 1962), we set up the basic formulas for the changes in the elastic constants. They are applied to the case of parabolic bands, where the analytic derivation can be carried very far in order to display important qualitative features such as the amplification: The relative change in the elastic constants may be more than a hundred times the number of holes pr. atom (the fractional impurity concentration). The quantitative results of this parabolic model are surprisingly bad even in cases where one would apriori expect the model to hold, e.g. in GaSb where the spin-orbit splitting is rather large. Nonparabolic effects are much stronger than anticipated. This more involved band model is taken into account by numerical computation, and the results, which for practical reasons are limited to the parameter d , compare favorably with other determinations for several materials.

After the completion of this work, the results of a similar

calculation for Si were published (Kim et al. 1976). However, the outcome is hampered by the use of obsolete valence-band parameters although our calculations shows that their results are somewhat better than stated by the authors.

Some spectacular, almost giant changes in the elastic constant C_{44} have been observed in doped p-type Si at very low temperatures (Mason and Bateman 1964). There has been no explanation so far. We propose a crude model with a hole bound to the acceptor doublet ground state. The observation and its interpretation illustrate that bound holes are not inactive in the present context, and they may also influence the data for higher temperatures.

Chapter 4 contains the determination of the optic deformation potential d_o as derived from the shift and broadening of the optic phonon resonance in Raman spectra with varying hole (acceptor) concentration. The measured shift and broadening may be related to the real and imaginary parts of the optic phonon self-energy which can be written up formally by reference to other texts. However, it was felt that a thorough basis should be included in the account so that secondary effects are more clearly exposed. Thus we derive the self-energy ab initio with a few shortcuts here and there, and the formal relationship to the free-energy results of the previous chapter is discussed. Computations for Si with nonparabolic bands yield shifts and broadenings which compare well with experimental data at 77K and 300K, so that a reasonably reliable value of d_o can be fixed. There are discrepancies at lower concentrations which are ascribed to specific impurity effects.

For Ge, the calculated broadening is an order of magnitude smaller than observed. To solve this problem, we investigate the effects of secondary hole scattering (with little success) and of the impurity distortions of the band structure. The latter effect is simulated by giving up momentum conservation in the hole-phonon interaction in the sense that the wave-vector dependence of the self-energy is calculated, and the

results are averaged over a typical impurity-state wave-vector range. The outcome resolves the dilemma for Ge so that we can be confident about the deducted value of d_0 .

The problem is now turned around and the effect of phonons on electronic excitation energies is studied in chapter 5, mainly for situations involving holes near the valence-band edge. The first part is a short account of the temperature dependence of the fundamental band gap, and based on recent work (Heine and Van Vechten 1976) we show the reciprocity of the phonon and electron/hole self-energy.

In the second part we investigate the self-energy of the spin-orbit splitting in the valence band as observable in the shifts and broadenings of the so-called E_0 and $E_0 + \Delta_0$ optical structures. Data for the broadening difference exist for many materials and are here analysed theoretically. The result is a value for a certain combination of the coupling constants for holes and optic phonons: The deformation potential d_0 and the multipole parameter a_1 . However, for physically reasonable values of a_1 , the multipole contribution turns out to be negligible, and so the experimental data yield only d_0 . For Ge, we then have two independent determinations of d_0 (phonon resonance shift on one hand and hole lifetime broadening on the other). The discrepancy between these two values is interpreted as direct spin-orbit contributions to the optic deformation potential.

The main conclusion as drawn in chapter 6 is that it is possible to extract detailed information on the electron-phonon coupling from the resonance spectra of phonons and electronic transitions. We have shown this for holes in particular materials where experimental data are available. The special band structure of holes is partly responsible for the effects, but its complicated nature has been a major obstacle previously. The complications have been overcome, and the resulting determination of coupling constants has mainly been limited by the lack of data.

The energy spectrum of electrons near the conduction-band

edge is less complicated, but then many of the effects studied here will either be absent or very small. A notable exception is intervalley scattering by short-wavelength phonons. We shall discuss how the present principles could furnish an independent determination of the coupling strength for individual phonons. For Si in particular, this might eventually resolve controversies of long standing.

One originally unexpected difficulty showed up during the investigations: The impurity concentrations needed for the large number of holes change the hole energy-level structure. From our results we tentatively conclude that the density-of-states is mainly modified in the vicinity of the band edge and that crystal momentum is no longer a good quantum number. It could have been much worse.

2. ENERGY LEVELS OF HOLES IN PURE AND DOPED SEMICONDUCTORS

The structure of the electronic energy levels near the top of the valence-band edge is complicated by degeneracy and spin-orbit effects. This feature is to some extent responsible for the effects to be studied in this work, and so one of the central points is an accurate treatment of details of this structure. Sec.2.1 describes the energy spectrum of holes as derived from $k \cdot p$ perturbation and defines the parabolic and nonparabolic models to be applied subsequently. Actual structures for Ge, Si, and related III-V compounds are used for an illustrative calculation of the variation of the chemical potential of holes as function of concentration and temperature.

Since the theory of the hole-phonon coupling is based on the deformation-potential concept, we discuss in Sec.2.2 the effects on the band structure of static homogeneous strains. This should elucidate the physical meaning of the deformation-potential parameters which are determined later on.

To avoid unnecessary details in the main text, Appendix A contains the analytic treatment of the nonparabolic band structure and its consequences for the general form of squared matrix elements. Appendix B summarizes the adiabatic approximation and the form of the electron-phonon interaction including multipole effects, and we work out the relevant expressions for the scattering matrix elements to be used in this work. A discussion of the screening of the electron-phonon interaction is included.

The hole-energy spectrum in p-doped semiconductors is the main topic of Sec.2.3 which also contains a short discussion of the possible direct effects of doping on the lattice spectrum. Secondary consequences of doping can usually be neglected, but here concentrations are of the order of 10^{20} cm^{-3} , and this represents an extraordinary situation in semiconductors. A careful examination of conventional concepts is needed.

2.1. Holes in parabolic and nonparabolic bands

The solution of the electronic eigenvalue problem for a lattice-periodic potential proceeds through the one-electron approximation to a band structure giving the energies $E(\vec{k})$ as function of wave vector $\vec{k}$ for the possible states of "one-electrons". We then fill up these single-particle levels according to the Fermi distribution allowing only one electron in each state (including spin).

In a pure semiconductor, an energy gap with no electron states exists between the highest-lying valence band and the conduction bands. At zero temperature, all states in the valence band are occupied and the conduction-band states empty. By doping with acceptor impurities, we are able to remove a few electrons from a region around the top of the valence band. Instead of accounting for the remaining incomplete valence-electron gas, it is convenient to consider the states with electrons missing as occupied by holes and to calculate the physical properties of these holes as if they have the inverse properties of the corresponding electron states. A rigorous basis for this concept can be found elsewhere. Throughout this work we shall take the hole energy as the inverse of the one-electron energy as sketched on Fig.2.1.

The band structure of holes near the valence-band edge is qualitatively similar in all diamond and zincblende type semiconductors of the $A^{N-8}B^8-N$ family (e.g. Ge, GaAs, ZnSe). Without spin, the band edge at $\vec{k}=0$ is a triply degenerate p-level of Γ_{25}' symmetry. Including spin and spin-orbit coupling, the edge is fourfold degenerate (Γ_8^+) with an adjacent double level (Γ_7^+) split off Δ_0 by the spin-orbit coupling. The situation is depicted on Fig.2.2.

Slightly away from $\vec{k}=0$, the bands are parabolic, i.e. $E \propto k^2$, but as a consequence of the degeneracy, E also depends on the direction $\hat{k}$ of $\vec{k}$ so that the surfaces of constant energy are warped. Further away, the three hole bands "interact" and the $E(\vec{k})$ - dependence is no longer parabolic. In the present

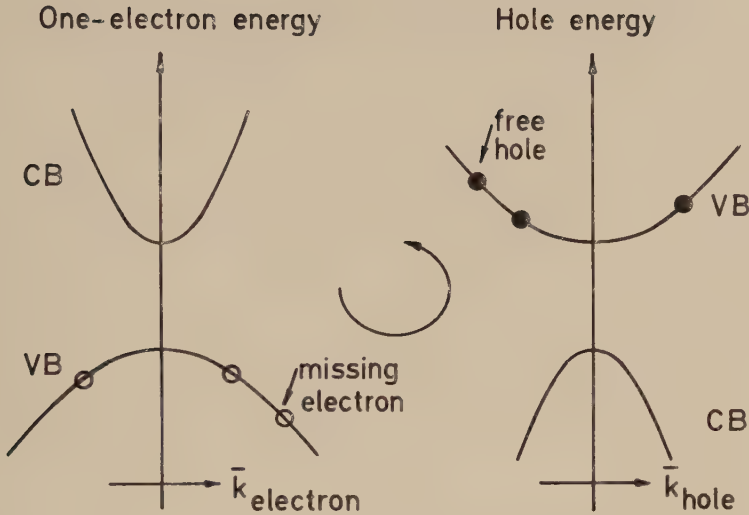


Figure 2.1. Simple one-electron band structure for a semiconductor with inverted bands on the right for hole description. CB and VB stand for the conduction and valence bands, respectively.

context the magnitudes of the hole chemical potential (Fermi energy) and/or thermal energies are comparable to Δ_0 so that effects of nonparabolicity are very important.

The quantitative problem is to solve the one-electron eigenvalue equation

$$H\psi = E\psi \quad (2-1)$$

so that the solutions E and ψ are sufficiently accurate for the valence bands near the edge. The Hamiltonian in the usual notation is

$$H = \frac{p^2}{2m} + V_0(\vec{r}) \quad (2-2)$$

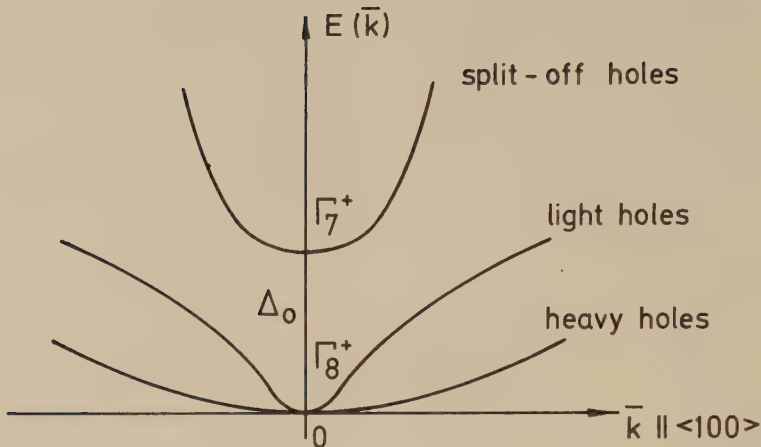


Figure 2.2. Hole-energy spectrum near $\bar{k}=0$ showing the three doubly degenerate bands and the spin-orbit splitting Δ_0 .

Its lattice periodicity makes it possible to define a $\bar{k}$ -vector as a "good quantum number". According to an original derivation (Luttinger and Kohn 1955), we choose the following basis set for the expansion of ψ :

$$|nj\bar{k}\rangle = \exp(i\bar{k}\cdot\bar{r}) |nj0\rangle \quad (2-3)$$

where $|nj0\rangle$ are eigenfunctions at $\bar{k}=0$, n numbers the eigenvalue $E_n(0)$, and j indicates linearly independent (degenerate) eigenfunctions. The Hamiltonian in this representation is

$$\begin{aligned} &\langle nj\bar{k} | H | n'j'\bar{k}' \rangle \\ &= \delta_{\bar{k}\bar{k}'} \left[\delta_{nn'} \delta_{jj'} (E_n(0) + \frac{\hbar^2 k^2}{2m}) + \frac{\hbar}{m} \langle nj0 | \bar{k} \cdot \bar{p} | n'j'0 \rangle \right] \end{aligned} \quad (2-4)$$

Second-order perturbation theory or a similar scheme may

eliminate the nondiagonal $\mathbf{k} \cdot \mathbf{p}$ terms and results in a contracted Hamiltonian matrix for a single basis energy $E_n(0)$ at $\bar{\mathbf{k}}=0$. For the actual case $\langle n_j 0 | \bar{\mathbf{p}} | n_j' 0 \rangle = 0$, and we find the reduced eigenvalue problem

$$\left[\bar{H}_n(\bar{\mathbf{k}}) - E_n(\bar{\mathbf{k}}) \bar{I} \right] \bar{F}_n(\bar{\mathbf{k}}) = 0 \quad (2-5)$$

$$\psi_n \approx \exp(i\bar{\mathbf{k}} \cdot \bar{\mathbf{r}}) \sum_j F_{nj}(\bar{\mathbf{k}}) |n_j 0\rangle \quad (2-6)$$

$$H_{n,jj'} = E_n(0) \delta_{jj'}$$

$$+ \sum_{\mathbf{r}_s} \mathbf{k} \cdot \mathbf{r}_s \frac{\hbar^2}{2m} \left[\delta_{jj'} \delta_{rs} + \frac{2}{m} \sum_{n'' \neq n} \frac{\langle n_j 0 | \mathbf{p}_r | n'' j'' 0 \rangle \langle n'' j'' 0 | \mathbf{p}_s | n_j' 0 \rangle}{E_n(0) - E_{n''}(0)} \right] \quad (2-7)$$

and $\bar{I}$ is unit matrix.

Without spin the three Γ'_{25} functions transform as $X\bar{y}z$, $Y\bar{v}zx$, and $Z\bar{v}xy$. In this case $\bar{H}$ has the 3×3 Shockley-matrix form (Shockley 1950) which we shall omit here.

Including spin, we have two complications: Two spin functions $\uparrow$ and $\downarrow$, and the spin-orbit coupling

$$H_{so} = \frac{\hbar}{4m^2 c^2} (\nabla V_0 \times \bar{\mathbf{p}}) \cdot \bar{\boldsymbol{\sigma}} \quad (2-8)$$

with $\bar{\boldsymbol{\sigma}}$ as the Pauli spin operator (and c the velocity of light). We may include H_{so} in our perturbation theory. At $\bar{\mathbf{k}}=0$, its inclusion results in a splitting Δ_0 of two energy levels Γ_8^+ and Γ_7^+ (see Fig. 2.3) with the following wave functions $|j\rangle$:

$$\begin{aligned} \Gamma_8^+ \quad |1\rangle &= \frac{1}{\sqrt{2}} (X + iY) \uparrow \\ |2\rangle &= \frac{1}{\sqrt{6}} [(X + iY) \downarrow - 2Z \uparrow] \\ |3\rangle &= \frac{1}{\sqrt{6}} [-(X - iY) \uparrow - 2Z \downarrow] \\ |4\rangle &= \frac{1}{\sqrt{2}} (X - iY) \downarrow \end{aligned} \quad (2-9)$$

$$\begin{aligned} \Gamma_7^+ \quad |5\rangle &= \frac{1}{\sqrt{3}} [(X+iY)\uparrow + Z\uparrow] \\ |6\rangle &= \frac{1}{\sqrt{3}} [-(X-iY)\uparrow + Z\uparrow] \end{aligned} \quad (2-10)$$

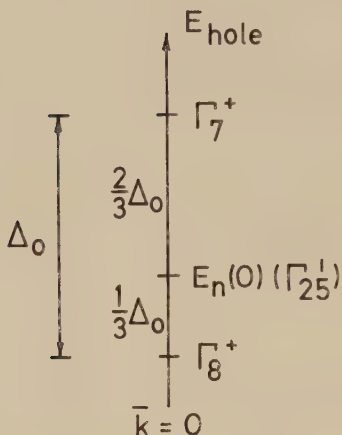


Figure 2.3. Level scheme showing the spin-orbit splitting of the original Γ'_{25} level at $\vec{k}=0$.

H_{SO} also gives a contribution to the $\vec{k} \cdot \vec{p}$ term in (2-4) which is derived by replacing $\vec{p}$ by $\vec{\pi}$:

$$\vec{\pi} = \vec{p} + \frac{\hbar}{4m^2c^2} (\vec{\sigma} \times \nabla V_0) \quad (2-11)$$

In polar materials, $\langle n_j 0 | \vec{\pi} | n_j' 0 \rangle \neq 0$ leads to linear terms in $\vec{k}$, but since these are extremely small, we shall not discuss this correction further.

Using the basis (2-9) and (2-10), we find the form of $\bar{H}$ in (2-7) as the following 6×6 matrix (Dresselhaus et al. 1955, Kane 1956, Bir and Pikus 1960):

$$\bar{H} = \begin{pmatrix} F & H & J & 0 & H/\sqrt{2} & J/\sqrt{2} \\ H^* & G & 0 & J & -(F-G)/\sqrt{2} & -H/\sqrt{3/2} \\ J^* & 0 & G & -H & -H^*/\sqrt{3/2} & (F-G)/\sqrt{2} \\ 0 & J^* & -H^* & F & -J^*/\sqrt{2} & H^*/\sqrt{2} \\ H^*/\sqrt{2} & -(F-G)/\sqrt{2} & -H/\sqrt{3/2} & -J/\sqrt{2} & \frac{1}{2}(F+G)+\Delta_0 & 0 \\ J^*/\sqrt{2} & -H^*/\sqrt{3/2} & (F-G)/\sqrt{2} & H/\sqrt{2} & 0 & \frac{1}{2}(F+G)+\Delta_0 \end{pmatrix} \quad (2-12)$$

with the quadratic k-dependent basic elements

$$\begin{aligned} \frac{2m_F}{\hbar^2} &= Ak^2 + \frac{1}{2}B(k_x^2 + k_y^2 - 2k_z^2) \\ \frac{2m_G}{\hbar^2} &= Ak^2 - \frac{1}{2}B(k_x^2 + k_y^2 - 2k_z^2) \\ \frac{2m_H}{\hbar^2} &= -D(k_x k_z - i k_y k_z) \\ \frac{2m_J}{\hbar^2} &= -\frac{\sqrt{3}}{2}B(k_x^2 - k_y^2) + i D k_x k_y \end{aligned} \quad (2-13)$$

Apart from Δ_0 , the matrix (2-12) has a very general form and symmetry which we shall encounter many times. We shall call it the extended Shockley form since it is a generalisation of the original Shockley matrix mentioned above.

A, B, and D are valence-band parameters. They are related to squared p matrix elements between the valence band-edge states (X, Y, Z) and conduction-band levels at $\vec{k}=0$, cf. eq. (2-7). It is shown elsewhere (Lawaetz 1971) that the valence-band parameters can be expressed in terms of contributions from different types of levels:

$$\begin{aligned} A &= -\frac{1}{3}(F_p + 2G_p + 2H_{1p} + 2H_{2p}) - 1 \\ B &= -\frac{1}{3}(F_p + 2G_p - H_{1p} - H_{2p}) \\ D/\sqrt{3} &= -\frac{1}{3}(F_p - G_p + H_{1p} - H_{2p}) \end{aligned} \quad (2-14)$$

(We have neglected the spin term "q" here. The relation to the so-called Luttinger parameters γ_1 , γ_2 , and γ_3 is $A=\gamma_1$, $B=2\gamma_2$, and $D/\sqrt{3}=2\gamma_3$. In this work we have reserved the notation γ for other purposes.) The origin of the quantities F_p , G_p , H_{1p} , and H_{2p} is shown schematically in Fig. 2.4.

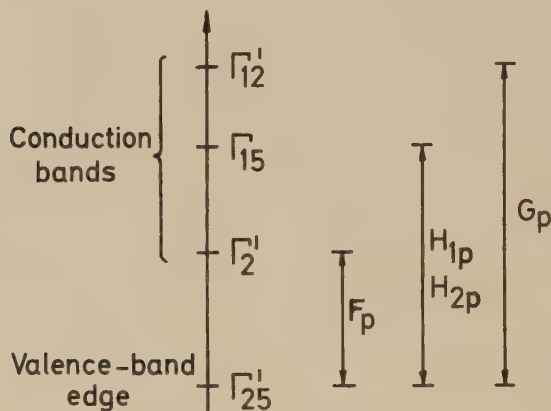


Figure 2.4. The relation between certain p matrix-element quantities F_p , ... and the one-electron energy levels at $k=0$. The Γ 's are symmetry notations.

The energy gap between $\Gamma_8^+(\Gamma_{25}')$ and $\Gamma_7^-(\Gamma_2')$ is usually called E_0 . For F_p we then find (Lawaetz 1971)

$$F_p = -\frac{E_p}{E_0} \quad (2-15)$$

where E_p is directly connected with the squared p matrix element. Actually (2-15) applies only to the valence-band parameters near the Γ_8^+ edge, the data cited in the literature. A more general version follows from the Löwdin (1951) approach

$$F_p = -\frac{E_p}{E_0 + E} \quad (2-16)$$

where E is the hole energy measured from the Γ_8^+ edge. The energy-dependent F_p in (2-16) will be necessary for the calculation of the $E_0 + \Delta_0$ broadening in Chapter 5. Elsewhere, the constant (2-15) will suffice. For H_p and G_p a similar correction is negligible because of the much larger gaps involved.

The actual values of the valence-band parameters have been determined experimentally with some reliability for Ge, Si, and GaAs, and with less accuracy for InP, GaP, GaSb, InSb, and ZnTe. Semiempirical values adjusted to Ge were calculated by the author (Lawaetz 1971). The most uncertain quantity is G_p , and we have recently corrected G_p values of the original work to improve the fit to available experimental data. The necessary corrections indicate that the $\Gamma_{25}' - \Gamma_{12}'$ energy gap is much smaller in polar materials than thought previously, and this feature has received some support from recent improved band calculations and high-energy spectra. Table 2.1 cites experimental and theoretical hole band-structure quantities. A direct comparison is not meaningful since the relevant quantities are certain sums and differences. The main discrepancy for the III-V compounds is the heavy-hole mass anisotropy which is overestimated by the theory. For consistency we have used the theoretical values in the following, but this makes very little difference in the results. Values for the II-VI compounds are rather uncertain, but the only ones available. We neglect the temperature dependence of these parameters throughout.

A critical parameter in the present work, where hole states far out in the nonparabolic region are relevant, is related to the limiting heavy-hole mass in the $\langle 110 \rangle$ direction:

$$\left(\frac{m}{m_{110}} \right)_{\text{large } k} = A + \frac{1}{2}B - \frac{3}{2} \frac{D}{\sqrt{3}} \quad (2-17)$$

Since no peculiarities of the valence-band structure have ever been observed, this quantity should be positive. This was not the case for older Si-data (Hensel and Fehrer 1963) and for some parameter sets in the author's original calcula-

tion (Lawaetz 1971) as well as for recent magneto-optical data (Hess et al. 1976) where this simple test should have been applied before claiming improvement. The present values are shown in Table 2.1. Insertion of (2-14) in (2-17) shows that G_p dominates this critical parameter which is therefore rather uncertain except for Si and Ge.

Equipped with these sets of band parameters we proceed to solve the eigenvalue equation (2-5) with the matrix $\bar{H}$ in (2-12). The parabolic case corresponds to $\Delta_0 \gg E$ and the well-known solutions

$$\frac{2m}{\hbar^2 k^2} E_\lambda = A \pm \left[B^2 + (D^2 - 3B^2) (\hat{k}_y^2 \hat{k}_z^2 + \hat{k}_z^2 \hat{k}_x^2 + \hat{k}_x^2 \hat{k}_y^2) \right]^{\frac{1}{2}} \quad (2-18)$$

or

$$E_\lambda^* \equiv \frac{\hbar^2 k^2}{2m} = E\beta_\lambda(\hat{k}) \quad \lambda=1,2 \quad (2-19)$$

$\beta_\lambda(\hat{k})$ is the effective-mass ratio for band λ in the direction $\hat{k}$, and E^* is the free-electron energy for the appropriate k .

$$\beta_\lambda^{-1}(\hat{k}) = A + e_\lambda \quad (2-20)$$

$$e_\lambda = (-1)^\lambda [\gamma_1 + \gamma_2]^{\frac{1}{2}} \quad (2-21)$$

$$\gamma_1 = B^2(1-3\mu_4) \quad , \quad \gamma_2 = D^2\mu_4 \quad (2-22)$$

$$\mu_4 = \hat{k}_y^2 \hat{k}_z^2 + \hat{k}_z^2 \hat{k}_x^2 + \hat{k}_x^2 \hat{k}_y^2 \quad (2-23)$$

(These expressions will reappear in many contexts.)

The nonparabolic case may be considered in two different ways depending on the type of hole property to be evaluated. We can solve either for the energy E with given $\hat{k}$ and E^* (i.e. k^2) or for E^* with given $\hat{k}$ and E . The former method applies to

Table 2.1. Quantities related to the valence-band parameters at zero temperature. Values for E_0 , Δ_0 , and E_p are from Lawaetz (1971) except where indicated. Type E and T stands for experimental resp. theoretical band parameters.

Material	E_0 (eV)	Δ_0 (eV)	E_p (eV)	Type	A	B	$D/\sqrt{3}$	$A+\frac{1}{2}B-\frac{3}{2}\frac{D}{\sqrt{3}}$
Ge	0.89	0.295	26.3	T	13.35	8.50	11.38	0.53
Si	4.20 ^b	0.044	21.6	E ^a	13.38	8.48	11.38	0.55
AlSb	2.30	0.645 ^d	18.7	T	4.22	0.78	2.88	0.29
Gap	2.87	0.078	22.2	E ^c	4.28	0.75	2.90	0.30
GaAs	1.52	0.34	25.7	T	4.48	2.36	3.34	0.65
				T	4.53	2.30	3.16	0.94
GaSb	0.81	0.77	22.4	T	7.98	5.16	6.40	0.96
InP	1.42	0.13	20.4	E ^e	6.98	4.40	5.67	0.68
				T	12.13	8.40	10.36	0.79
InAs	0.42	0.38	22.2	T	6.61	4.50	5.36	0.82
InSb	0.24	0.81	23.1	E ^f	5.04	3.12	3.45	1.43
ZnS	3.80	0.070	20.4	T	20.00	17.08	18.42	0.91
ZnSe	2.82	0.43	24.2	T	35.41	31.62	33.66	0.73
ZnTe	2.39	0.92	19.1	T	2.87	1.84	2.02	0.76
CdTe	1.60	0.91	20.7	T	4.10	2.82	3.18	0.74
				T	4.07	2.48	3.12	0.63
				T	5.62	4.12	4.76	0.54

a Hensel and Suzuki (1969) and (1974).
b Aspres and Studna (1972).
c Hensel (1970). Similar values are found by Owner-Petersen and Samuelsen (1968) assuming $H_{2p} = 0$.
d Rustagi et al. (1976).
e Skolnick et al. (1976).
f Leotin et al. (1974).

situations with long-wavelength phonon shift and broadening where vertical hole transitions are involved. The latter procedure is relevant for the sampling of properties related to surfaces of constant hole energy and will be used in Chapter 5. It has the additional advantage that the Löwdin-type re-normalization (2-16) can be included exactly.

In both cases, which are treated in Appendix A, we express the solution as a generalisation of the parabolic case (2-19):

$$E^* = E\beta_{\lambda}(E, \hat{k}) \quad \lambda = 1, 2, 3 \quad (2-24)$$

and the related quantities α and $\tilde{\alpha}$ given by

$$\beta_{\lambda}^{-1} = A - \alpha_{\lambda} \quad (2-25)$$

$$\tilde{\alpha} = \frac{\Delta_0}{E^*} \quad (2-26)$$

To illustrate the actual solution, we have carried out calculations of the hole concentration p as function of the chemical potential μ . This relation will be useful later where the thermal-equilibrium distribution of holes enters. For unit volume we have

$$p = 2 \sum_{\lambda \bar{k}} f(E_{\lambda}(\bar{k})) \quad (2-27)$$

where f is the Fermi distribution

$$f(E) = \left[\exp\left(\frac{E - \mu}{k_0 T}\right) + 1 \right]^{-1} \quad (2-28)$$

T is the temperature and k_0 the Boltzmann constant. As in standard textbooks the sum over $\bar{k}$ in (2-27) may be transformed into integrals

$$p = N_0(T) \frac{1}{4\pi} \int d^2k \frac{2}{\sqrt{\pi}} \int_0^{\infty} \left(\frac{E^*}{k_0 T} \right)^{\frac{1}{2}} d \left(\frac{E^*}{k_0 T} \right) \sum_{\lambda} f(E_{\lambda}) \quad (2-29)$$

$$N_0(T) = 2(2\pi m k_0 T)^{-2} \cdot 3/2 = 2,5 \cdot 10^{19} \left(\frac{T}{300K} \right)^{3/2} \text{cm}^{-3} \quad (2-30)$$

Eq. (2-29) is applied directly for the nonparabolic case where E_{λ} is found as function of E^* and $\hat{k}$. For the parabolic case (2-29) may be simplified to

$$p = N_0 \tilde{D}_0 F_{\frac{1}{2}} \left(\frac{\mu}{k_0 T} \right) \quad (2-31)$$

where $\tilde{D}_0$ is the combined density-of-states factor for light and heavy holes:

$$\begin{aligned} \tilde{D}_0 &= \frac{1}{4\pi} \int d^2k \sum_{\lambda=1}^2 \beta_{\lambda}^{3/2}(\hat{k}) \\ &= \frac{1}{4\pi} \int d^2k \sum_{\lambda=1}^2 (A + e_{\lambda})^{-3/2} \end{aligned} \quad (2-32)$$

and $F_{\frac{1}{2}}$ is one of the Fermi integrals

$$F_{\frac{1}{2}}(y) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{x^{\frac{1}{2}} dx}{\exp(x-y)+1} \quad (2-33)$$

This function is tabulated (Blakemore 1962). Values of $\tilde{D}_0$ for selected materials have been calculated numerically from the parameters in Table 2.1 and are shown in Table 2.2.

A formula similar to (2-31) can be found for the nonparabolic case:

Table 2.2. Parabolic density-of-states factor $\tilde{D}_0$ for holes in selected semiconductors as calculated from theoretical band parameters in Table 2.1.

Material	$\tilde{D}_0$ (2-32)
Ge	0.216
Si	0.450
GaAs	0.373
GaSb	0.267

$$p = N_0 \cdot \frac{2}{\sqrt{\pi}} \int_0^{\infty} \tilde{D}(E=k_0 T x) \frac{x^{\frac{1}{2}} dx}{\exp(x - \frac{\mu}{k_0 T}) + 1} \quad (2-34)$$

where the energy-dependent total density-of-states factor is derived in Appendix A, eq. (A-17)

$$\tilde{D}(E) = \frac{1}{4\pi} \int d^2 k \sum_{\lambda} \beta_{\lambda}^{3/2} \left[1 - \frac{\alpha^2 - e^2}{3\alpha^2 - 3e^2 + 2\alpha\tilde{\alpha}} \cdot \frac{\tilde{\alpha}}{A - \alpha} \right]_{\lambda, E}^{-1} \quad (2-35)$$

$\beta_{\lambda}^{3/2}$ is understood to be nonzero only for real values, i.e., there is no $\lambda=3$ contribution for $E < \Delta_0$.

For $\mu \ll -k_0 T$, the region of nondegenerate hole distributions, eq.(2-34) can be cast in the form (2-31) with $\tilde{D}_0$ replaced by a temperature-dependent effective density-of-states factor $\langle \tilde{D}(T) \rangle$

$$\langle \tilde{D}(T) \rangle = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \tilde{D}(E=k_0 T x) x^{\frac{1}{2}} \exp(-x) dx \quad (2-36)$$

To demonstrate the extraordinary effects of nonparabolicity in Si, Table 2.3 shows calculated values of $\langle \tilde{D}(T) \rangle$. The dominant effect is the extreme behavior of the heavy-hole band

in the $\langle 110 \rangle$ direction. The results are very important for intrinsic carrier concentrations (Gagliani and Reggiani 1975), but the present work will employ degenerate distributions where the above concept is less meaningful.

Table 2.3. Effective density-of-states factor for holes in nondegenerate Si.

T(K)	0	77	300
$k_B T / \Delta_0$	0.00	0.15	0.59
$\langle D(T) \rangle$	0.450	0.620	1.005
$\langle D(T) \rangle / D_0$	1.00	1.38	2.23

Results of computations of the chemical potential as function of hole concentration for a number of relevant materials are shown in Figs. 2.5 and 2.6. Despite the band singularity at $E = \Delta_0$, the curves exhibit a smooth behaviour, and the similarity between Ge, GaAs, and GaSb is remarkable by contrast to Si. Realistic maximum doping levels are of the order of $5 \cdot 10^{20} \text{ cm}^{-3}$, so that the chemical potential or Fermi level may reach values up to 300 meV. For this high-energy range, the results may be somewhat inaccurate for Ge, GaAs, and GaSb since the calculations were based on the band-edge parameters such as (2-15) with no adjustment like in (2-16) as relevant for these materials with direct gaps E_0 of order 1 eV.

2.2. Effects of static strain

The influence of homogeneous deformation on the hole-energy spectrum was studied systematically by Pikus and Bir (1959). The essence of their results is that the matrix elements of the deformation-potential energy in the valence-band basis states (and to first order in strain) can be represented by a Shockley matrix so that the total $\bar{k}$ - and strain(ϵ)-dependent Hamiltonian matrix is given by (2-12) with the following

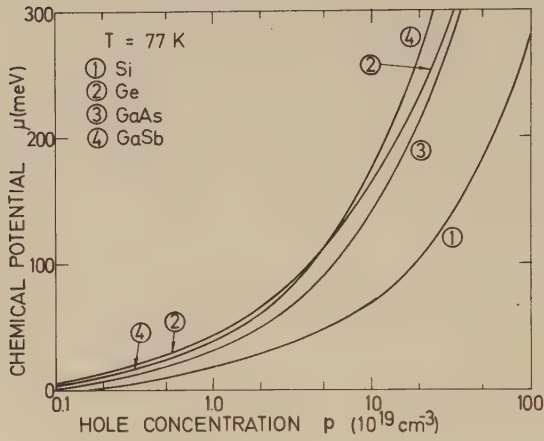


Figure 2.5. Chemical potential vs. hole concentration at 77K for 4 semiconductor materials.

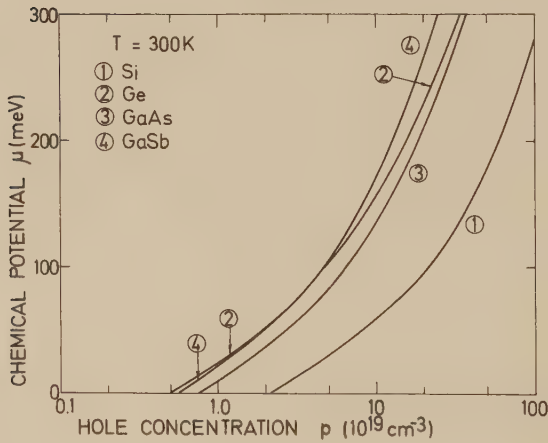


Figure 2.6. Chemical potential vs. hole concentration at 300K for 4 semiconductor materials.

generalisation: $D_{ij}^{k_1 k_j} \rightarrow D_{ij}^{k_1 k_j} + d_{ij} \epsilon_{ij}$, where ϵ_{ij} is a strain component and d_{ij} a deformation potential (constant). The conservation of overall cubic symmetry then yields

$$\begin{aligned} AE^* &\rightarrow AE^* + a(\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}) \\ \frac{1}{2}B(\hat{k}_x^2 + \hat{k}_y^2 - 2\hat{k}_z^2)E^* &\rightarrow \frac{1}{2}B(\hat{k}_x^2 + \hat{k}_y^2 - 2\hat{k}_z^2)E^* + \frac{1}{2}b(\epsilon_{xx} + \epsilon_{yy} - 2\epsilon_{zz}) \\ \frac{\sqrt{3}}{2}B(\hat{k}_x^2 - \hat{k}_y^2)E^* &\rightarrow \frac{\sqrt{3}}{2}B(\hat{k}_x^2 - \hat{k}_y^2)E^* + \frac{\sqrt{3}}{2}b(\epsilon_{xx} - \epsilon_{yy}) \\ D\hat{k}_y\hat{k}_zE^* &\rightarrow D\hat{k}_y\hat{k}_zE^* + d\epsilon_{yz} \text{ etc.} \end{aligned} \quad (2-37)$$

For the parabolic region of the band structure where an analytic solution (2-18)-(2-20) exists, we can apply the generalisation (2-37) directly to find the band structure in the strained crystal. (2-18) is written as

$$\begin{aligned} \frac{E_\lambda(\bar{k})}{E^*} &= A + (-1)^\lambda \left\{ \left[\frac{1}{2}B(\hat{k}_x^2 + \hat{k}_y^2 - 2\hat{k}_z^2) \right]^2 + \left[\frac{\sqrt{3}}{2}B(\hat{k}_x^2 - \hat{k}_y^2) \right]^2 \right. \\ &\quad \left. + \left[D\hat{k}_y\hat{k}_z \right]^2 + \left[D\hat{k}_z\hat{k}_x \right]^2 + \left[D\hat{k}_x\hat{k}_y \right]^2 \right\}^{\frac{1}{2}} \end{aligned} \quad (2-38)$$

and so using (2-37)

$$E_\lambda(\bar{k}, \epsilon) = AE^* + a\text{Tr}(\epsilon) + (-1)^\lambda (E_{kk}^2 + E_{ke}^2 + E_{\epsilon\epsilon}^2)^{\frac{1}{2}} \quad (2-39)$$

$$E_{kk}^2 = E^{*2} e^2$$

$$\begin{aligned} E_{ke}^2 &= E^* B b \left[(\hat{k}_y^2 - \hat{k}_z^2)(\epsilon_{yy} - \epsilon_{zz}) + \text{c.p.} \right] \\ &\quad + 2E^* D d \left[\hat{k}_y \hat{k}_z \epsilon_{yz} + \text{c.p.} \right] \end{aligned}$$

$$E_{\epsilon\epsilon}^2 = \frac{1}{2}b^2 \left[(\epsilon_{yy} - \epsilon_{zz})^2 + \text{c.p.} \right] + d^2 \left[\epsilon_{yz}^2 + \text{c.p.} \right] \quad (2-40)$$

and c.p. means cyclic permutation of xyz.

The term $a\text{Tr}(\epsilon)$ represents a common shift of the band structure with dilatation and will not interest us here. The b and d terms will produce a splitting ΔE_{12} of the initial degeneracy at $k=0$:

$$\Delta E_{12} = E_2(0, \epsilon) - E_1(0, \epsilon) = 2E_{\epsilon\epsilon} \quad (2-41)$$

This provides us with a simple physical interpretation of the deformation potentials b and d. For a uniaxial strain in the $\langle 001 \rangle$ -direction, $-2\epsilon_{xx} = -2\epsilon_{yy} = \epsilon_{zz} = \epsilon_{001}$, the splitting is

$$\Delta E_{12}(001) = 3|b\epsilon_{001}| \quad (2-42)$$

Similarly for a $\langle 111 \rangle$ -strain $\epsilon_{yz} = \epsilon_{zx} = \epsilon_{xy} = \epsilon_{111}$, and

$$\Delta E_{12}(111) = \sqrt{3}|d\epsilon_{111}| \quad (2-43)$$

For $k > 0$ and very small strains we find the following shifts in the band structure (by second-order expansion of (2-39))

$$\delta E_{\lambda}(\vec{k}, \epsilon) = \frac{E_{k\epsilon}^2}{2e_{\lambda}E^*} + \left[\frac{E_{\epsilon\epsilon}^2}{2e_{\lambda}E^*} - \frac{(E_{k\epsilon}^2)^2}{8e_{\lambda}^3E^{*3}} \right] \quad (2-44)$$

The first term is linear in strain whereas the bracket is quadratic, i.e.

$$\delta E_{\lambda}(\vec{k}, \epsilon) = \delta E_{\lambda}^{(1)} + \delta E_{\lambda}^{(2)} \quad (2-45)$$

These small-strain expressions could also have been deduced by perturbation theory. This is what we will do for the non-parabolic case. Denoting the strain perturbation by δV , we find

$$\delta E_{\lambda}^{(1)} = \langle \lambda \vec{k} | \delta V | \lambda \vec{k} \rangle ; \quad \delta E_{\lambda}^{(2)} = \sum_{\lambda' \neq \lambda} \frac{|\langle \lambda \vec{k} | \delta V | \lambda' \vec{k} \rangle|^2}{E_{\lambda} - E_{\lambda'}} \quad (2-46)$$

As in appendix A and B for similar matrix elements, these expressions should be summed over "final" spin states with common $(\lambda, \bar{k})$ and averaged over "initial" states with common $(\lambda, \bar{k})$.

In the above theory we have considered only effects which are initially linear in strain, although the final result contains second-order terms as well. We show later that they are of equal importance. Direct quadratic terms in the strain Hamiltonian (and zero order in k) may also play a role. They must have complete cubic symmetry and are thus diagonal in the Shockley matrix just as $a\text{Tr}(\epsilon)$. The result is a common shift of all bands

$$\delta E_{\lambda}^{(2)}(\text{direct}) = \frac{1}{2} b_2' (\epsilon_{yy} - \epsilon_{zz})^2 + d_2' \epsilon_{yz}^2 + \text{c.p.} \quad (2-47)$$

The principal difference between $\delta E_{\lambda}^{(2)}$ in (2-44) and in (2-47) is that the former has opposite sign for the two bands (in general for the nonparabolic case $\sum_{\lambda} \delta E_{\lambda}^{(2)} = 0$ whereas the latter is independent of λ and $\bar{k}$).

The strain associated with a long-wavelength optic vibration is purely internal in the sense that the two sublattices move relative to each other. From the displacements $\bar{u}_1$ and $\bar{u}_2$ of the two sublattices we define the optic strain

$$u_o \bar{e} = (\bar{u}_1 - \bar{u}_2) / a_c \quad (2-48)$$

where $\bar{e}$ is a unit vector and a_c the lattice constant. The change $\delta \bar{r}_b$ in the bond vector corresponding to such a deformation in the bond direction is

$$\delta \bar{r}_b = u_o a_c \bar{e}_{111} \quad (2-49)$$

The same change can be produced by a macroscopic strain ϵ_{111}

$$\begin{aligned} \delta \bar{r}_b &= \bar{\epsilon} \bar{r}_b = \frac{1}{4} a_c \begin{Bmatrix} 0 & \epsilon & \epsilon \\ \epsilon & 0 & \epsilon \\ \epsilon & \epsilon & 0 \end{Bmatrix} \begin{Bmatrix} 1 \\ 1 \\ 1 \end{Bmatrix} \\ &= \frac{\sqrt{3}}{2} \epsilon_{111} a_c \bar{e}_{111} \end{aligned} \quad (2-50)$$

Thus the same bond-length change is achieved for

$$\frac{1}{2} u_o = \frac{\sqrt{3}}{4} \epsilon_{111} \quad (2-51)$$

(This is only formally true since we have neglected that there is also an explicit internal strain associated with the macroscopic strain).

The band splitting at $k=0$ for the (111)-strain was shown in (2-43). We can then define the optic deformation potential d_o so that

$$\Delta E_{12} = \frac{1}{2} u_o d_o = \sqrt{3} \epsilon_{111} d \quad (2-52)$$

The analogy between (111)-strain and optic strain will be used when we compare the formulas for the changes in elastic constants and optic frequency. If (2-51) is used for replacing $\frac{\sqrt{3}}{4} \epsilon_{111}$ by $\frac{1}{2} u_o$, (2-52) shows that $\frac{1}{4} d_o$ should replace d . The definition (2-52) of d_o is identical to the one given in (B-15) since this corresponds to

$$\begin{aligned} d\epsilon_{yz} &\sim \frac{1}{2} u_o d_o e_{osx} \\ d\epsilon_{111} &\sim \frac{\sqrt{3}}{4} \epsilon_{111} d_o \frac{1}{\sqrt{3}} \\ d &\sim \frac{1}{4} d_o \end{aligned} \quad (2-53)$$

Apart from the above similarity in the definitions of deformation potentials, there is also a more practical consequence of the analogy between the perturbations due to (111)-strain and optic strain: The energy and angular dependence of the

average squared matrix elements are identical in the two situations. In this respect we can establish a correspondence between the parabolic $(\delta E_{\lambda}^{(1)})^2$ and $\delta E_{\lambda}^{(2)}$ on the one side and the squared matrix elements $|H_{\lambda\lambda'}^O(\vec{k})|^2$ (B-19) for optic phonon transitions with zero wave vector on the other. This correspondence is then continued to the nonparabolic region, which is solved for the optic phonon case in Appendix B. It follows that the general matrix elements of δV in (2-46) can be derived for (111)-strains and used for the calculation of the change in the elastic constant C_{44} which is related to this type of strain.

2.3. Doping effects

An essential feature in the method with phonon and elastic constant renormalisation is the variation of the free-hole concentration. This is brought about by controlled doping with special impurities, but at high levels of doping, we expect side effects to become substantial: changes in the free-hole energy spectrum as well as in the phonon spectrum. In the present section we shall discuss these effects qualitatively. As typical examples we consider boron-doped Si (Si:B) and gallium-doped Ge (Ge:Ga) with special emphasis on the former.

A single B-acceptor in Si produces a localized hole state 46 meV below the band edge (in the hole-energy picture). This is the acceptor ground state and is fourfold degenerate just as the band edge. In addition we have excited states, but they do not concern us here except for one particular level, namely the spin-orbit satellite which is about 23 meV above the ground state. This will be important for the bound-hole contribution to the elastic constants as treated in Sec. 3.3, and appropriate references are given there.

The spatial extension of the ground state is typically an effective Bohr radius a_B . The wave function is constructed by linear combination of free-hole states with k-vectors inside a radius $\sim 2\pi/a_B$. In this region, a band state has

disappeared, but this is of no consequence at low impurity concentrations.

At higher acceptor concentrations of Si:B, the ionisation energy is observed to decrease at about 10^{18} cm^{-3} , and it vanishes at $7 \cdot 10^{18} \text{ cm}^{-3}$ (Pearson and Bardeen 1949). The most simple explanation is that envelope wave functions of the states on neighboring B-atoms now overlap and the single-energy ground states develop into a band. When this band overlaps with the valence-band edge, there is no activation energy needed any more. This model is to some extent equivalent to saying that the linear combinations of free-hole states used for the bound states become coupled at high doping, since only a limited concentration of states is available with $k \leq 2\pi/a_B$. This alternative model shows the additional feature that an appreciable concentration of free-hole states has been "used up" and so the free-hole energy spectrum is distorted near the band-edge. A different and perhaps supplementary interpretation is based on the fact that a large concentration of free holes will screen the impurity potential so that the ionisation energy finally disappears (Bonch-Bruyevich 1966).

In any case the impurities are distributed at random. The distortions of the band structure are consequently followed by mixing of k -states because the lattice periodicity is destroyed. We believe that this k -state mixing occurs in the active region from which the impurity wave functions are constructed.

The qualitative conclusions on the impurity effects on the hole-band structure are thus: (1) The wave vector $\bar{k}$ is no longer a good quantum number for $k \leq 2\pi/a_B$, and (2) some of the low-energy free-hole states are shifted to energies below the band edge with the consequence that the chemical potential is smaller and band-energy differences at a definite $\bar{k}$ are greater than calculated from the intrinsic band structure. At the highest acceptor concentrations, the chemical potential will be well above the distortions of the energy

spectrum and so the effects of band-edge modifications will be minor.

For Ge:Ga the isolated-acceptor binding energy is 11.3 meV and the critical concentration is much smaller ($\sim 5 \cdot 10^{17} \text{ cm}^{-3}$). The band-edge distortion may thus be smaller, and the k-vector mixing may be the most prominent effect. We shall return to this point in Sec. 4.4.

The large impurity concentrations are relevant for the phonon renormalization problem. So far we have discussed the indirect influence, i.e. through the effects on the hole-band structure. However, the impurities may have a more direct influence on the mechanical properties of the crystal, the phonon spectrum.

An acceptor produces a localized hole level outside the valence band. Similarly, an impurity atom, which is lighter than the atoms of the host crystal (e.g. Si:B), will bring about a localized vibrational state with frequency outside the intrinsic spectrum (Dawber and Elliott 1963, Maradudin 1966). This state is strongly localized in the sense that its amplitude falls off drastically within a few atomic distances from the impurity. It can therefore be thought of as made up of combinations of intrinsic states with wave vectors $\vec{q}$ from a broad range in the Brillouin zone. Consequently, we expect no specific distortion of the "band edge", the optic phonon with $q \sim 0$. However, shifts and broadenings of the optic phonon could still be of the relative order of the fractional impurity concentration.

In addition to the localized states, the impurities may mix the intrinsic phonon states so that $\vec{q}$ is no longer well defined. Thus the Raman spectrum should exhibit a continuum down to zero energy shift because an excitation with $\vec{q} \sim 0$ couples to most of the phonon spectrum. Model calculations for 1% carbon in Si (Maradudin 1966) show that the principal effect is a small asymmetric broadening of the intrinsic Raman peak. Again, the effects are proportional to the impurity content, and 1% Si:B corresponds roughly to $4 \cdot 10^{20} \text{ cm}^{-3}$,

the highest concentrations used in this work. A direct influence of impurities on the results is therefore believed to be unimportant since the electronic contributions are enhanced relative to a fractional effect.

For Ge:Ga, there is no localized state because the mass difference is too small. Furthermore, the Ge-crystal itself contains an appreciable spread of isotropic masses, and particular effects due to the Ga-impurities are washed out entirely.

3. INFLUENCE OF HOLES ON ELASTIC CONSTANTS

The effects of free carriers on the elastic constants were first studied by Keyes (1961) with main emphasis on electrons. Since then, much data have been accumulated on p-type materials, but a detailed quantitative interpretation has been lacking. This situation is repaired by the work described in the present chapter.

The slopes of the acoustic phonon spectrum $\omega = \omega(\vec{k})$ for $k \rightarrow 0$ are the sound velocities which are simply related to the elastic constants of the material. The ordinary elastic constants as measured by static or quasistatic (ultrasonic) techniques do not, however, reflect phonon properties which are adiabatic, but rather the isothermal response of the medium. The distinction between isothermal and adiabatic properties is related to the possible relaxation of the background so that low frequencies permit such a relaxation whereas high frequencies do not. The difference between the two types of elastic constants in semiconductors is due to anharmonic lattice effects or free carriers. Isothermal properties are derived from free-energy considerations.

The strain-induced change in the hole contribution to the free energy is the subject of Sec. 3.1. In Sec. 3.2 this theory is applied to the model with free holes in parabolic bands where an analytic description makes it possible to get qualitative insight. Coefficients depending on the band parameters are computed numerically, and the results for the elastic-constant change with free holes are compared with existing experimental data, however, with a rather negative outcome. As evident from the subsequent treatment, this discrepancy is caused by nonparabolicity.

The formalism of the parabolic model is adapted to bound-hole effects in Sec. 3.3. At low temperatures and relatively low impurity concentrations, the holes are bound to the acceptors, but even then a rather strong effect on the elastic constants occurs. The analysis of a limited set of experimental

data indicates an elastic instability. ($C_{44} \rightarrow 0$), and a theoretical model with compensation is shown to account reasonably well for these features.

Finally, Sec. 3.4 deals with the change in the elastic constant C_{44} as brought about by holes in nonparabolic bands. The following comparison between theory and experiment leads to deformation potentials d which are in very good agreement with values determined by other techniques.

3.1. Free energy and elastic properties

The thermodynamic equilibrium of the crystal is determined by minimum free energy F . For a displacement $\bar{u}$ at the position $\bar{x}$ the strain ϵ_{ij} is defined as

$$\epsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \quad (3-1)$$

The increase in elastic energy due to a deformation ϵ from equilibrium has the following form for a cubic crystal:

$$\delta F = \frac{1}{2} C_{11} \epsilon_{xx}^2 + C_{12} \epsilon_{yy} \epsilon_{zz} + 2C_{44} \epsilon_{yz}^2 + \text{c.p.} \quad (3-2)$$

δF is here pr. unit volume. The C_{ij} are the elastic constants. The above expression is conveniently reorganised according to the symmetry of the three main types of deformation in a cubic material: (a) volume change $\text{Tr}(\epsilon)$, (b) tetrahedral deformation ($\epsilon_{yy} - \epsilon_{zz}$) and c.p., and (c) trigonal deformation ϵ_{yz} and c.p.. We then find

$$\begin{aligned} \delta F = & \frac{1}{6} (C_{11} + 2C_{12}) (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})^2 \\ & + \frac{1}{6} (C_{11} - C_{12}) [(\epsilon_{yy} - \epsilon_{zz})^2 + \text{c.p.}] \\ & + 2C_{44} [\epsilon_{yz}^2 + \text{c.p.}] \end{aligned} \quad (3-3)$$

The contribution of the carriers to the free energy will (of course) turn out to be of similar form so that it is possible

to derive carrier-induced changes like δC_{44} directly. In the following, we take $\text{Tr}(\epsilon) = 0$ since free carriers in bands with a common dilatational shift do not change the bulk modulus.

The free energy of holes at the temperature T is (from standard statistical mechanics)

$$F_h = \mu N_h + k_O T \sum_k \ln(1-f_k) \quad (3-4)$$

where N_h is the number of holes, μ their chemical potential, k indicates the hole state, and f_k is the probability for the state k to be occupied by a hole in thermal equilibrium

$$f_k = \left[\exp\left(\frac{E_k - \mu}{k_O T}\right) + 1 \right]^{-1} \quad (3-5)$$

E_k is the energy of the state k , and k includes the spin state.

A homogeneous deformation changes the energies E_k and the chemical potential μ , but not the number of carriers:

$$N_h = \sum_k f_k \quad (3-6)$$

Then to second order

$$0 = \delta N_h = \sum_k \frac{df}{dE_k} (\delta E_k - \delta \mu) + \frac{1}{2} \sum_k \frac{d^2 f}{dE_k^2} (\delta E_k - \delta \mu)^2 \quad (3-7)$$

In order to find the change $\delta \mu^{(1)}$ linear in strain, the last term can be neglected, and so

$$\delta \mu^{(1)} = \frac{\sum_k \frac{df}{dE_k} \delta E_k^{(1)}}{\sum_k \frac{df}{dE_k}} \quad (3-8)$$

For a uniaxial strain ($\text{Tr}(\epsilon) = 0$) $\delta E_k^{(1)}$ has the same symmetry in $\bar{k}$ -space as the strain because their combination in $\delta E_k^{(1)}$ has full cubic symmetry. As an example we refer to the

parabolic case eqs. (2-40), (2-44), and (2-45). Then for any function $g(E_k)$ having cubic symmetry

$$\sum_k g(E_k) \delta E_k^{(1)} = 0 \quad (3-9)$$

and consequently (3-8) yields

$$\delta \mu^{(1)} = 0 \quad (3-10)$$

The second-order change $\delta \mu^{(2)}$ will be of no interest.

For the free energy (3-4), the change to second order is

$$\begin{aligned} \delta F_h &= N \delta \mu + \frac{1}{2} N (\delta \mu)^2 - k_O T \sum_k (1-f)^{-1} \frac{df}{dE} (\delta E_k - \delta \mu) \\ &\quad - \frac{1}{2} k_O T \sum_k \frac{d}{dE} \left[(1-f)^{-1} \frac{df}{dE} \right] (\delta E_k - \delta \mu)^2 \\ &= N \delta \mu + \frac{1}{2} N (\delta \mu)^2 + \sum_k f_k (\delta E_k - \delta \mu) \\ &\quad + \frac{1}{2} \sum_k \frac{df}{dE} (\delta E_k - \delta \mu)^2 \end{aligned} \quad (3-11)$$

where we have used that (3-5) yields

$$k_O T (1-f)^{-1} \frac{df}{dE} = -f \quad (3-12)$$

Now we apply (3-6) and (3-10) together with $\sum_k f_k \delta E_k^{(1)} = 0$ from (3-9), and we find to second order in strain

$$\delta F_h = \sum_k f_k \delta E_k^{(2)} + \frac{1}{2} \sum_k \frac{df}{dE} (\delta E_k^{(1)})^2 \quad (3-13)$$

This expression was derived by Bir and Tursunov (1962). The first term is clearly the change in the internal energy of the holes, and so the last term is connected with the change in entropy ($\delta F = \delta E - T \delta S$).

The validity of (3-13) may break down in two ways related to the assumptions of (a) isothermal and (b) local equilibrium. If we increase the frequency of the ultrasonic wave we get out of the isothermal region where $\omega\tau \ll 1$, τ being a characteristic redistribution time of the holes. On the other side with $\omega\tau > 1$, we approach the adiabatic region, where the entropy term has vanished. Indeed, this is exactly what we find later in the high-frequency case where our arguments are based on the self-energy concept (Chapter 4). The local approximation is valid for $q\ell \ll 1$ (ℓ is essentially the hole mean-free path), i.e. for long wavelengths. The relation always holds in the situations studied in this work.

How do we know when the isothermal approximation is no longer good? Its breakdown is connected with absorption, and so one indicator is high absorption. Another and safer way is to make sure that the measured changes in elastic constants are independent of frequency. The problem turns out to be relevant for low-temperature experiments which we encounter in connection with the bound-hole contribution in Sec. 3.3.

3.2. Free holes in parabolic bands

With the expectation that the two-parabolic-band model will be a reasonable approximation for certain ranges of temperature and hole concentration, we work out this model because it has the major advantage of analytic expressions for $\delta E_k^{(1)}$ and $\delta E_k^{(2)}$.

We insert (2-44) and (2-45) in (3-13) observing that index k in the latter covers band index λ , wave vector $\vec{k}$, and spin.

$$\delta F_h = 2 \sum_{\lambda \vec{k}} \left\{ f(E_\lambda) \frac{\pi_{12}}{2e_\lambda E^*} + \frac{1}{2} \frac{df}{dE_\lambda} \pi_{11} \right\} \quad (3-14)$$

where we have introduced the E^* -independent quantities

$$\pi_{11} = \frac{(E_{kE}^2)^2}{4e E^{*2}} \quad (3-15)$$

$$\pi_{12} = E_{\varepsilon\varepsilon}^2 - \frac{(E_{k\varepsilon}^2)^2}{4eE^{*2}} \quad (3-16)$$

The sum over $\bar{k}$ is transformed into an integral over $\bar{k}$ -space, here most conveniently E^* and $\hat{k}$. Pr. unit volume we obtain similar to (2-29)

$$\begin{aligned} \delta F_h = N_O(T) \frac{1}{4\pi} \int d^2k \frac{2}{\sqrt{\pi}} \int_0^\infty \left(\frac{E^*}{k_O T} \right)^{\frac{1}{2}} d \left(\frac{E^*}{k_O T} \right) \\ \times \sum_\lambda \left\{ f(E_\lambda) \frac{\pi_{12}}{2e_\lambda E^*} + \frac{1}{2} \frac{df}{dE_\lambda} \pi_{11} \right\} \end{aligned} \quad (3-17)$$

Using the band structure $E^* = E\beta_\lambda(\hat{k})$ and the relation

$$\int_0^\infty dE E^{\frac{1}{2}} \frac{df}{dE} = -\frac{1}{2} \int_0^\infty dE E^{-\frac{1}{2}} f \quad (3-18)$$

we find

$$\begin{aligned} \delta F_h = \frac{2N_O}{k_O T} \frac{1}{4\pi} \int d^2\hat{k} \sum_\lambda \beta_\lambda^{3/2} \left[\frac{\pi_{12}}{2e_\lambda \beta_\lambda} - \frac{\pi_{11}}{4} \right] \\ \times \frac{1}{\sqrt{\pi}} \int_0^\infty \left(\frac{E}{k_O T} \right)^{-\frac{1}{2}} d \left(\frac{E}{k_O T} \right) f(E) \end{aligned} \quad (3-19)$$

The last integral is tabulated similar to (2-33):

$$F_{-\frac{1}{2}}(y) = \frac{1}{\sqrt{\pi}} \int_0^\infty \frac{x^{-\frac{1}{2}} dx}{\exp(x-y)+1} \quad (3-20)$$

so that (3-19) becomes

$$\begin{aligned} \delta F_h = \frac{2N_O}{k_O T} F_{-\frac{1}{2}} \left(\frac{\mu}{k_O T} \right) \frac{1}{4\pi} \int d^2\hat{k} \sum_\lambda \beta_\lambda^{3/2} \left[\frac{\pi_{12}}{2e_\lambda \beta_\lambda} - \frac{\pi_{11}}{4} \right] \\ = - \frac{p}{4k_O T} \frac{F_{-\frac{1}{2}}}{F_{+\frac{1}{2}}} \frac{1}{4\pi D_O} \int d^2\hat{k} \sum_\lambda \beta_\lambda^{3/2} \left[-\frac{4\pi_{12}}{e_\lambda \beta_\lambda} + 2\pi_{11} \right] \end{aligned} \quad (3-21)$$

where we have inserted the hole concentration p from (2-31).

The angular integration in (3-21) selects the parts of π_{11} and π_{12} which have full cubic symmetry. From (3-15), (3-16), (2-44), and (2-45) the cubic parts (with index c) are easily found to be

$$2\pi_{11c} = (\epsilon_{yy} - \epsilon_{zz})^2 b^2 \frac{\gamma_1}{2(\gamma_1 + \gamma_2)} + 2\epsilon_{yz}^2 d^2 \frac{\gamma_2}{3(\gamma_1 + \gamma_2)} + c.p. \quad (3-22)$$

$$2\pi_{12c} = (\epsilon_{yy} - \epsilon_{zz})^2 b^2 \left[1 - \frac{\gamma_1}{2(\gamma_1 + \gamma_2)} \right] + 2\epsilon_{yz}^2 d^2 \left[1 - \frac{\gamma_2}{3(\gamma_1 + \gamma_2)} \right] + c.p. \quad (3-23)$$

where γ_1 and γ_2 are $\hat{k}$ -dependent quantities defined in (2-22). We observe that F_h now has the same strain dependence as

F in (3-3), and a comparison of the two expressions then yields the relative changes in the elastic constants

$$[C_s \equiv \frac{1}{2}(C_{11} - C_{12})]$$

$$\frac{\delta C_s}{C_s} = - \frac{p}{4k_o T} \frac{3b^2}{C_s} \frac{F_{-\frac{1}{2}}}{F_{+\frac{1}{2}}} \alpha_b \quad (3-24)$$

$$\frac{\delta C_{44}}{C_{44}} = - \frac{p}{4k_o T} \frac{d^2}{C_{44}} \frac{F_{-\frac{1}{2}}}{F_{+\frac{1}{2}}} \alpha_d \quad (3-25)$$

with

$$\alpha_b = \frac{1}{4\pi D_o} \int d^2k \sum_{\lambda} \beta_{\lambda}^{3/2} \left\{ - \frac{2}{e_{\lambda} \beta_{\lambda}} \left[1 - \frac{\gamma_1}{2(\gamma_1 + \gamma_2)} \right] + \frac{\gamma_1}{2(\gamma_1 + \gamma_2)} \right\} \quad (3-26)$$

$$\alpha_d = \frac{1}{4\pi D_o} \int d^2k \sum_{\lambda} \beta_{\lambda}^{3/2} \left\{ - \frac{2}{e_{\lambda} \beta_{\lambda}} \left[1 - \frac{\gamma_2}{3(\gamma_1 + \gamma_2)} \right] + \frac{\gamma_2}{3(\gamma_1 + \gamma_2)} \right\} \quad (3-27)$$

The formulas (3-24) and (3-25) are similar to the ones derived by Bir and Tursunov (1962) except that α_b and α_d are now given without the spherical approximation used in that work.

Since $\tilde{D}_0 \sim \beta^{3/2}$ and $\beta_\lambda^{-1} = A + e_\lambda$, α_b and α_d depend only on the two band-parameter ratios B/A and $D/\sqrt{3}A$. Once α_b and α_d have been calculated for a certain material, the evaluation of δC_s and δC_{44} is straightforward.

The analytical formulas (3-24) and (3-25) show how the free-carrier contribution to the elastic constants varies with concentration and temperature. In the nondegenerate region $F_{-\frac{1}{2}}/F_{+\frac{1}{2}} = 1$, and so $-\delta C/C \propto p/k_O T$. In the degenerate region $F_{-\frac{1}{2}}/F_{+\frac{1}{2}} \propto k_O T/\mu$ and $\mu \propto p^{2/3}$, so that $-\delta C/C \propto p^{1/3}$ and independent of temperature. This behavior is sketched in Fig. 3.1.

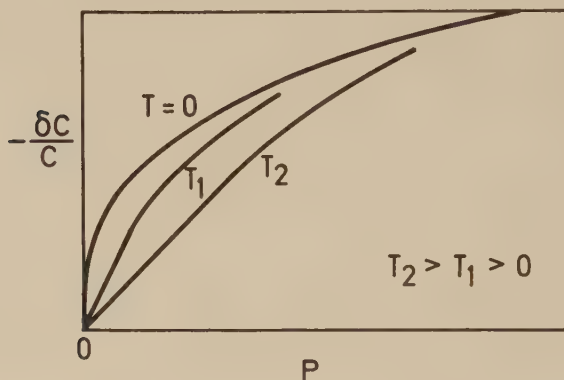


Figure 3.1 Qualitative dependence of free-carrier contribution δC to elastic constant C on temperature T and hole conc. p .

A very important feature of the present free-carrier contribution to the elastic constant is the enhancement, i.e. each acceptor-produced hole contributes relatively much more than its fractional share. Let N be the atomic concentration of the crystal. Put $\alpha \approx 1$ and $F_{-\frac{1}{2}}/F_{+\frac{1}{2}} \approx 1$ for a nondegenerate

distribution. (3-25) then gives

$$- \frac{\delta C_{44}}{C_{44}} \approx \frac{p}{N} \cdot \frac{Nd^2}{4C_{44}k_o T} \quad (3-28)$$

where the last factor is the enhancement. Insertion of typical values and $T = 300K$, this factor comes out to be about 20, and it could be much larger at lower temperatures.

We can also compare this "first-order" effect with the direct "second-order" effect following the quadratic term in the band-structure change with strain, eq. (2-47). This latter contribution $\delta C^{(2)}$ is directly proportional to the hole concentration, and we find the ratio

$$\frac{\delta C^{(1)}}{\delta C^{(2)}} \approx \frac{d^2}{k_o T d_2'} \quad (3-29)$$

For a normal behavior we expect $d_2' \sim d$, and so the enhancement here is $\sim d/k_o T$ or about 100 at room temperature. For a degenerate carrier distribution (high concentrations) $k_o T$ is replaced by the chemical potential $\mu \propto p^{2/3}$, and so the enhancement drops off with increasing concentration.

The evaluation of the band-structure parameters α_b and α_d according to (3-26) and (3-27) is performed numerically, and the results will be presented as contour maps with coordinates

$$x^2 = \left(\frac{B}{A}\right)^2, \quad y^2 = \left(\frac{D}{\sqrt{3}A}\right)^2 \quad (3-30)$$

For the valence-band edge to be at $k = 0$, we have $0 \leq x^2 < 1$ and $0 \leq y^2 < 1$. The spherical case with $x = y$ can be handled analytically:

$$\alpha_b = \alpha_d = \frac{1}{5} \left[\frac{8}{x} \frac{(1+x)^{3/2} - (1-x)^{3/2}}{(1+x)^{3/2} + (1-x)^{3/2}} - 7 \right] \quad (3-31)$$

which corresponds to the result obtained by Bir and Tursunov (1962) with slight modifications. The flat-band limiting cases can also be worked out exactly:

$$x^2 = 1 : \alpha_b = \frac{1}{2}, \quad \alpha_d = 0 \quad (3-32)$$

$$y^2 = 1 : \alpha_b = 0, \quad \alpha_d = \frac{1}{3} \quad (3-33)$$

whereas the point $(x^2, y^2) = (1, 1)$ leaves α_b and α_d undefined. Near $(0, 0)$ the contours are straight lines

$$\alpha_b \approx 1 - \frac{1}{4}x^2 - \frac{3}{4}y^2, \quad \alpha_d \approx 1 - \frac{1}{2}x^2 - \frac{1}{2}y^2 \quad (3-34)$$

The numerical results are shown in Figs. 3.2 and 3.3. Useful material values are collected in Table 3.1. Most of them will be used later for a comparison with results obtained for a nonparabolic band structure. Here we use a selection for a preliminary comparison with experimental data. For Si we show how the derived values of b and d vary with hole concentration as a consequence of the shortcomings of the parabolic

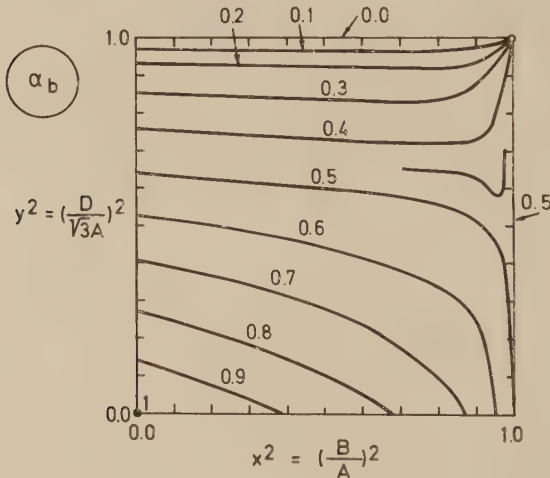


Figure 3.2. Contour diagram of parameter α_b in δC_s .

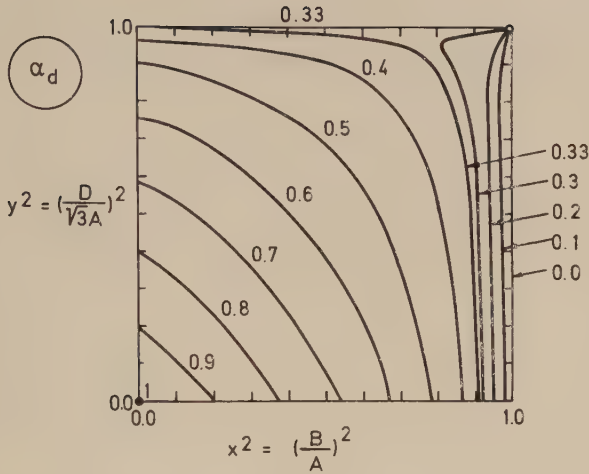


Figure 3.3. Contour diagram of parameter α_d in δC_{44} .

Table 3.1. Material values of α_b , α_d , and density-of-states factor D_o .

Material	Ge	Si	GaAs	GaSb
A	13.35	4.55	7.98	12.13
B	8.50	0.78	5.16	8.40
$D/\sqrt{3}$	11.38	2.88	6.40	10.36
x^2	0.40	0.03	0.42	0.48
y^2	0.72	0.46	0.64	0.73
α_b	0.41	0.65	0.47	0.40
α_d	0.51	0.76	0.54	0.48
$\tilde{D}_o$	0.216	0.450	0.373	0.267

model, and even for GaSb, where the relatively large spin-orbit splitting would indicate the validity of the approximation, the values of b and d differ considerably from results of other types of experiment.

Table 3.2. Derivation of b from data on δC_s for Si at 77K using the parabolic model. The data are from Csavinszky and Einspruch (1963). $C_s = 5.09 \cdot 10^{10} \text{ Nm}^{-2}$.

$\frac{p}{10^{19} \text{ cm}^{-3}}$	$\frac{\mu}{1 \text{ meV}}$	$-\frac{\delta C_s}{C_s} \cdot 10^3$	$\frac{b}{1 \text{ eV}}$
0.32	10.3	2.6	2.46
1.4	35.2	8.5	3.17
11.	143.	38.	4.66

Table 3.3. Derivation of d from data on δC_{44} for Si at 77K using the parabolic model. The data are from Mason and Bateman (1963) (first entry) and from Fjeldly et al. (1973) (all others). $C_{44} = 7.96 \cdot 10^{10} \text{ Nm}^{-2}$.

$\frac{p}{10^{19} \text{ cm}^{-3}}$	$\frac{\mu}{1 \text{ meV}}$	$-\frac{\delta C_{44}}{C_{44}} \cdot 10^3$	$\frac{d}{1 \text{ eV}}$
0.25	7.6	2.5	5.25
0.6	18.6	5.8	6.25
2.6	54.0	19.5	8.44
7.0	106.	33.1	9.35
16.	184.	49.4	9.97

For silicon at $T = 77K$, the experimental and theoretical data are shown in Tables 3.2 and 3.3. The resulting b and d should be compared with the optical determination by Laude et al. (1971): $b = (2.1 \pm 0.1) \text{ eV}$ and $d = (4.85 \pm 0.15) \text{ eV}$. Obviously, the parabolic two-band model underestimates the effect to a considerable extent. One might suggest the possibility of deriving the true values of b and d by extrapolation to $p = 0$, but as we shall see in Sec. 3.3, this procedure is not justified because the experimental data at the lower concentrations do not represent the effects of free holes in the valence bands of the pure crystal. Thus the data for $|\delta C_{44}|$ should have been about 50% higher!

For GaSb with $\Delta_0 = 0.77 \text{ eV}$, we expect the parabolic model to be much better. The existing data were obtained by Kупenko et al. (1973) at 293K for $p = 3.9 \cdot 10^{19} \text{ cm}^{-3}$. The results are shown in Table 3.4. They should be compared with $b = 2.2 \text{ eV}$ and $d = 4.6 \text{ eV}$ found by Guillaume and Lavallard (1970). Again the parabolic model underestimates the effect appreciably.

Table 3.4. Derivation of b and d from data on δC_s and δC_{44} for GaSb at $T = 293K$ (here calculated for 300K) using the parabolic model. $C_s = 2.40 \cdot 10^{10} \text{ Nm}^{-2}$, $C_{44} = 4.32 \cdot 10^{10} \text{ Nm}^{-2}$. Data are from Kупenko et al. (1973).

$\frac{p}{10^{19} \text{ cm}^{-3}}$	$\frac{\mu}{1 \text{ meV}}$	$-\frac{\delta C_s \cdot 10^3}{C_s}$	$-\frac{\delta C_{44} \cdot 10^3}{C_{44}}$	$\frac{b}{1 \text{ eV}}$	$\frac{d}{1 \text{ eV}}$
3.9	95.	14.8	8.8	3.71	6.07

In order to prepare for the theory in the following sections, we shall reformulate the "parabolic" result (3-25) for the elastic-constant change δC_{44} so that the road is open for generalisations to more complex situations. The purpose is to formulate the free energy F_h (3-13) and the constant δC_{44} in terms of perturbation expressions for the energy

shifts δE , cf. eq. (2-46). Thus for the present $\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz} = 0$. As a starting point we take (3-14) and notice that the cubic parts π_{11c} and π_{12c} can be written as

$$\begin{aligned}\pi_{11c} &= d^2 g_{11} (\epsilon_{yz}^2 + \epsilon_{zx}^2 + \epsilon_{xy}^2) \\ \pi_{12c} &= d^2 g_{12} (\epsilon_{yz}^2 + \epsilon_{zx}^2 + \epsilon_{xy}^2)\end{aligned}\quad (3-35)$$

where g_{11} and g_{12} are given by (B-27) for the parabolic case. The correspondence is relevant because the π 's represent squared matrix elements as in (2-46). Furthermore $2e_\lambda E^* = E_\lambda - E_{\lambda' \neq \lambda}$ and so (3-14) becomes

$$\delta F_h = 2d^2 \sum_{\lambda=1}^2 \sum_k \left\{ \sum_{\lambda' \neq \lambda} \frac{f(E_\lambda)}{E_\lambda - E_{\lambda'}} g_{\lambda\lambda'} + \frac{1}{2} \frac{df}{dE_\lambda} g_{\lambda\lambda} \right\} (\epsilon_{yz}^2 + \epsilon_{zx}^2 + \epsilon_{xy}^2) \quad (3-36)$$

or by reference to (3-3):

$$\delta C_{44} = d^2 \sum_{\lambda k} \left\{ \sum_{\lambda' \neq \lambda} \frac{f(E_\lambda)}{E_\lambda - E_{\lambda'}} g_{\lambda\lambda'} + \frac{1}{2} \frac{df}{dE_\lambda} g_{\lambda\lambda} \right\} \quad (3-37)$$

where it has been used that $g_{11} = g_{22}$ and $g_{12} = g_{21}$. We see from eq. (3-37) that there is a simple distinction between interband and intraband contributions, and that the latter is the entropy term.

The above formula is useful for the generalisation to the nonparabolic case by replacing the parabolic $g_{\lambda\lambda'}$ by its nonparabolic counterpart already found in Appendix B. It can also be applied to the impurity problem in the following section. There we are interested in the $k \rightarrow 0$ behavior.

3.3. Bound holes

Most of the early experimental interest in the change δC of the elastic constants effected by free carriers was prompted by studies of acoustic attenuation where simplified

theories indicated that δC entered directly the formula for absorption. Apparently for this reason Mason and Bateman (1963) measured C_{44} for heavily doped p-Si as function of temperature down to very low temperatures. Typical results are shown in Fig. 3.4, and we observe a drastic drop indicating $|\delta C_{44}| \propto T^{-1}$. No explanation has so far appeared. The net acceptor (boron) concentration is $2.5 \cdot 10^{18} \text{ cm}^{-3}$, and so all holes are frozen in on the acceptor states for $T < 20\text{K}$. We conclude that bound holes may contribute significantly to the elastic constants, and we shall propose a semiquantitative explanation of the strange behavior of δC_{44} .

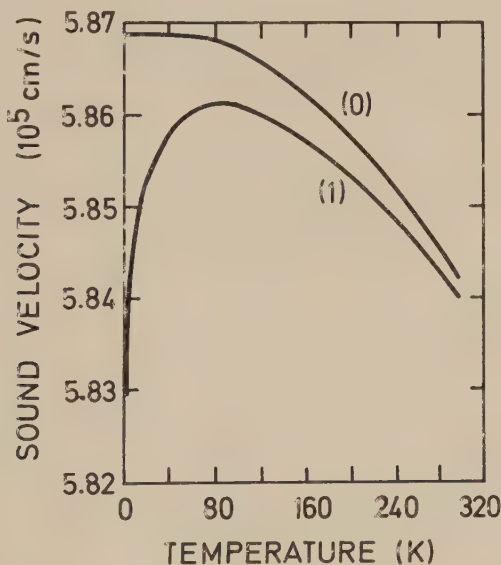


Figure 3.4. Sound velocity $(C_{44}/\rho)^{1/2}$ (where ρ is the mass density) measured at 20 MHz for (0) pure and (1) doped Si ($2.5 \cdot 10^{18} \text{ cm}^{-3}$). Diagram redrawn from Mason and Bateman (1963).

The existing data are collected in two papers (Mason and Bateman 1963 and 1964) and refer to three crystals with different impurity content. However, most of the data are hampered by

strong absorption which is essentially proportional to the frequency squared, and so in most cases the measuring frequency is not the same for high and low temperatures. A set of such data are plotted versus T^{-1} in Fig. 3.5, and we observe that no simple interpretation can be worked out.

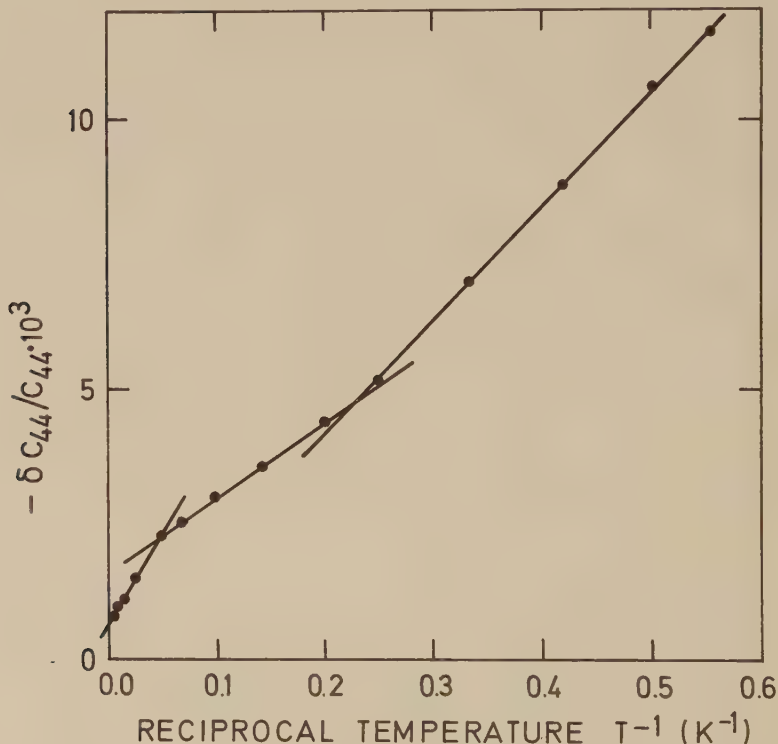


Figure 3.5. Analysis of experimental data for elastic constant change for sample with impurity (boron) content $5 \cdot 10^{17} \text{ cm}^{-4}$. The frequency change occurred around $T = 6\text{K}$. Data from Mason and Bateman (1964), where points shown here are read from Fig. 8(b) curve B.

On the other hand, the curve in Fig. 3.4 was measured at a generally lower frequency (20 MHz), and these data may thus be more representative of the static (isothermal) elastic constant. The corresponding data are listed in Table 3.5 and plotted in Fig. 3.6. It is a pity that the temperature range does not extend below 5K, but anyway, the results might then again be affected by frequency dependent effects. Fig. 3.6 shows that the low-temperature data ($T < 25K$) are represented by the formula

$$- \frac{\delta C_{44}}{C_{44}} \cdot 10^3 = 3.2 + \frac{50K}{T} \quad (3-38)$$

for the net acceptor concentration $2.5 \cdot 10^{18} \text{ cm}^{-3}$. Deviations from this behavior at higher temperatures can be ascribed to de-freezing of the bound holes since (3-38) will be explained below as a bound-hole property.

Table 3.5 Reproduction of table from Mason and Bateman (1963) of elastic constant change for an impurity concentration of $2.5 \cdot 10^{18} \text{ cm}^{-3}$.

T (K)	$-\delta C_{44} (10^8 \text{ Nm}^{-2})$	$-\frac{\delta C_{44}}{C_{44}} \cdot 10^3$
5	10.50	13.20
10	6.47	8.13
20	4.54	5.70
30	3.80	4.77
50	2.56	3.22
80	2.02	2.54
100	1.80	2.26
300	0.74	0.93

The model proposed for the interpretation of (3-38) is based on two features: The degeneracy of the acceptor ground state and the assumed presence of compensating donors.

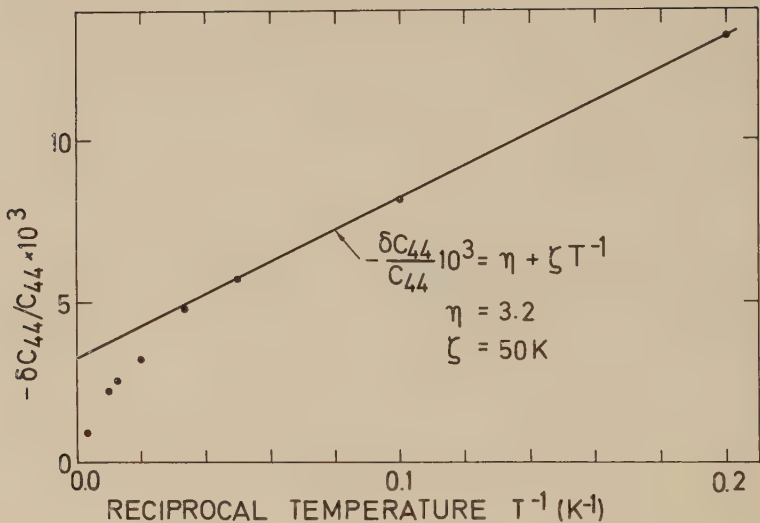


Figure 3.6. Analysis of data shown in Table 3.5 for a crystal with impurity concentration $2.5 \cdot 10^{18} \text{ cm}^{-3}$. Inspection of the original reference (Mason and Bateman 1963) shows that the trends are followed by many more data points.

The lowest acceptor level is a doublet, and its splitting and shift with strain follows that of the band edge, however with somewhat different deformation potentials b' and d' for the linear splitting, and with a quadratic shift resulting from "interaction" with the spin-orbit satellite. The boron-acceptor spin-orbit splitting is $\Delta_B = 23 \text{ meV}$ (Wright and Mooradian 1967, Chandrasekhar et al. 1976, Baldereschi and Lipari 1976).

In order to establish a formula for δC_{44} we redesign eq. (3-37) to suit our present impurity problem. All holes are assumed to be either in the acceptor ground state or in compensating donor states which do not contribute to δC_{44} in Si. For an acceptor concentration N_A and a state occupation factor f_A , we make the replacements $d \rightarrow d'$ and

$$2 \sum_{\vec{k}} f(E_A(\vec{k})) \rightarrow \frac{1}{2} N_A f_A \quad (3-39)$$

so that (3-37) becomes

$$\delta C_{44} = \frac{1}{4} d'^2 N_A \sum_{\lambda=1,2} \left\{ \frac{f_A}{-\Delta_B} g_{\lambda 3} + \frac{1}{2} \frac{df_A}{dE_A} \sum_{\lambda' \neq \lambda} g_{\lambda \lambda'} \right\} \quad (3-40)$$

where $g_{\lambda \lambda'}$ is taken as the $k \rightarrow 0$ limit of the corresponding band-structure factors in (B-37):

$$g_{\lambda 3} = 1, \quad g_{\lambda 1} + g_{\lambda 2} = 1 \quad (3-41)$$

Furthermore,

$$f_A = \left[\frac{1}{4} \exp\left(\frac{E_A - \mu}{k_O T}\right) + 1 \right]^{-1} \quad (3-42)$$

$$\frac{df_A}{dE_A} = - \frac{1}{k_O T} f_A (1 - f_A) \quad (3-43)$$

The result is

$$- \frac{\delta C_{44}}{C_{44}} = \frac{d'^2}{2 \Delta_B C_{44}} N_A f_A + \frac{d'^2}{4 k_O T C_{44}} N_A f_A (1 - f_A) \quad (3-44)$$

For an uncompensated semiconductor at low temperatures, μ is situated about halfway between the band edge and the acceptor energy E_A so that $f_A = 1$. It follows that the first term in (3-44) is constant and the second term zero. This situation does not agree with the experimental behavior (3-38). Assuming a certain compensation by donors N_D , μ will be close to E_A and $f_A(1-f_A)$ consequently different from zero. Since

the occupation numbers are constant as long as we can disregard free holes, we have

$$N_A f_A = N_A - N_D, \quad N_A f_A (1 - f_A) = (N_A - N_D) \frac{N_D}{N_A} \quad (3-45)$$

and the apparent net acceptor concentration N'_A is $N_A - N_D$. Eq. (3-44) then takes the form

$$-\frac{\delta C_{44}}{C_{44}} = \frac{d'^2}{2\Delta_B C_{44}} N'_A + \frac{d'^2}{4k_{OTC_{44}}} N'_A \cdot \frac{N_D}{N_A} \quad (3-46)$$

which is in qualitative agreement with the experimental results.

We can also try to analyse for quantitative agreement. Chandrasekhar et al. (1976) have determined $d' \sim 4.2$ eV for boron acceptors (in accord with earlier results). Using $C_{44} = 7.96 \cdot 10^{10} \text{ Nm}^{-2}$ and $N'_A = 2.5 \cdot 10^{18} \text{ cm}^{-3}$, the comparison of (3-38) and (3-46) yields $\Delta_B = 13.8$ meV and $N_D/N_A = 0.19$. The deduced compensation is not unreasonable, but Δ_B is somewhat smaller than the actual spin-orbit splitting of 23 meV. This is not a serious discrepancy because we have neglected all excited states other than the spin-orbit satellite, and the theory also disregards impurity-banding effects which should be present at these concentrations. We add that the analysis covers one crystal, and that its impurity content was characterised by its room temperature conductivity only.

The theoretical result (3-46) is the consequence of the symmetry-induced degeneracy of the acceptor ground state and does not in itself contain any limit for the change in C_{44} when going to ultra-low temperatures. In principle, this implies an impurity-induced structural instability where the crystal behaves like butter when subjected to quasi-static deformations.

In practice, there will always be local strain fluctuations which split the degeneracy. Resonant acoustic absorption experiments (Schad and Lassmann 1976) show typical fluctuation splittings to be 0.1 meV in Si. Since k_{OT} is 0.1 meV at 1K, we expect the softening to level off at this temperature.

The acoustic properties of p-Si for $N_A' \approx 1.5 \cdot 10^{19} \text{ cm}^{-3}$ have been investigated experimentally by Kadyshevich et al. (1967), but the data for $|\delta C_{44}|$ at ordinary temperatures are about three times higher than found by Fjeldly et al. (1973), discussed in the next section. The data are thus extremely unreliable and are not discussed further except that nothing singular shows up at low temperatures (4.2K). With due reservation we can say that this is also to be expected since at this impurity concentration, the bound-hole states have merged with the valence band so that no acceptor ground state exists. Finally, we emphasize that bound holes contribute significantly to the change in elastic constants. For impurity concentrations in Si below $7 \cdot 10^{18} \text{ cm}^{-3}$ (where the ionisation energy vanishes) we expect considerable freeze-in of free holes even at 77 and 300K. From (3-25) and (3-46) we estimate the ratio of contributions from a single hole

$$\frac{(\delta C_{44})_{\text{bound hole}}}{(\delta C_{44})_{\text{free hole}}} \approx \left(\frac{d'}{d}\right)^2 \frac{k_o T}{\Delta_B} \quad (3-47)$$

which is of order one. It follows that freeze-in has only quantitative influence on the results, a feature actually observed in the next section. The neglect of freeze-in in the interpretation may lead to erroneous conclusions.

3.4. Free holes in nonparabolic bands

The application of equation (3-37) to the nonparabolic case is now straightforward since we just have to insert the proper energy levels and the g-factors given in Appendix B, eq. (B-25). The band indices λ and λ' cover 1, 2, and 3, i.e. the spin-orbit split-off band is included. The formula is made suitable for numerical computation by insertion of

$$\frac{df}{dE} = - \frac{1}{k_o T} f(1-f) \quad (3-48)$$

$$2 \sum_{\vec{k}} \dots = N_O \frac{1}{4\pi} \int d^2 \vec{k} \frac{2}{\sqrt{\pi}} \int_0^\infty d \left(\frac{E}{k_O T} \right)^* \left(\frac{E}{k_O T} \right)^{\frac{1}{2}} \dots \quad (3-49)$$

and eq. (3-37) becomes

$$- \frac{\lambda C_{44}}{C_{44}} = \frac{N_O d^2}{4 k_O T C_{44}} \cdot \frac{1}{4\pi} \int d^2 \vec{k} \frac{2}{\sqrt{\pi}} \int_0^\infty d \left(\frac{E}{k_O T} \right)^* \left(\frac{E}{k_O T} \right)^{\frac{1}{2}} \times \sum_{\lambda=1}^3 \sum_{\lambda' \neq \lambda} \left\{ \frac{2 k_O T f(E_\lambda)}{E_\lambda - E_{\lambda'}} g_{\lambda\lambda'} + f(E_\lambda) \left[1 - f(E_\lambda) \right] g_{\lambda\lambda} \right\} \quad (3-50)$$

Then for a certain material and temperature the procedure is to choose the chemical potential μ and calculate the corresponding values of

$$X_P = \frac{P}{10^{19} \text{ cm}^{-3}} \quad (3-51)$$

and

$$Y_{44} = - \frac{\delta C_{44}}{C_{44}} \cdot 10^3 \quad (3-52)$$

which will come out in practical orders of magnitude. Taking Si-parameters ($C_{44} = 7.96 \cdot 10^{10} \text{ Nm}^{-2}$, $d = 4.85 \text{ eV}$) as basis, we find the front factor in Y_{44} (3-52) and (3-50) to be

$$\frac{N_O d^2}{4 k_O T C_{44}} \cdot 10^3 = 11.45 \left(\frac{T}{300K} \right)^{\frac{1}{2}} \left(\frac{d}{4.85 \text{ eV}} \right)^2 \left(\frac{C_{44}}{7.96 \cdot 10^{10} \text{ Nm}^{-2}} \right)^{-1} \quad (3-53)$$

The formula for p was shown in eq. (2-29).

For each material, we calculate the results for $T = 77K$ and $300K$. At $77K$ we compare with similar "parabolic" results of Sec. 3.2 which can be cast in the practical form:

$$X_P(\text{par.}) = 2.50 \left(\frac{T}{300K} \right)^{3/2} \tilde{D}_O F_{\frac{1}{2}} \left(\frac{\mu}{k_O T} \right) \quad (3-54)$$

$$Y_{44}(\text{par.}) = \frac{N_O d^2}{4k_{TC} 44} \cdot 10^3 \cdot D_O \alpha_d F_{-\frac{1}{2}} \left(\frac{\mu}{k_O T} \right) \quad (3-55)$$

The relative change in the other elastic constant $\delta C_s / C_s$ will be given by a formula analogous to eq. (3-50). However, the g-factors are different, and we have not worked them out because our primary purpose is not to derive the acoustic deformation potentials by the present method. Rather we are interested in checking the method on the acoustic case before proceeding to the high-frequency case in the next section. The analysis of δC_{44} is thus sufficient. A reasonable guess on the value of the deformation potential b can be made on the assumption that the effects of nonparabolicity are much the same for Y_{44} and $Y_s = -\delta C_s / C_s \cdot 10^3$. A combination of nonparabolic and parabolic formulas then yields the scaling

$$b^2 \approx d^2 \left[\frac{1}{3} \frac{C_s}{C_{44}} \cdot \frac{\alpha_d}{\alpha_b} \left(\frac{Y_s}{Y_{44}} \right) \exp. \right] \quad (3-56)$$

where d is the value fitted to Y_{44} , and Y_s and Y_{44} refer to the same temperature and hole concentration.

Silicon

In addition to the band parameters and derived quantities given previously, we use $C_{44} = 7.96 \cdot 10^{10} \text{ Nm}^{-2}$ ($C_s = 5.09 \cdot 10^{10} \text{ Nm}^{-2}$) and $d = 4.60 \text{ eV}$ (which will be found as the best fit). Tables 3.6, 3.7, and 3.8 contain the result of computations, and Table 3.9 gives the experimental data on Y_{44} . This is all plotted in Fig. 3.7.

Inspection of this diagram shows that there is a pronounced difference between the results of the parabolic and nonparabolic models, a feature to be expected for silicon. Furthermore, the agreement between theory and experiment is not that good at first sight, but actually, the serious discrepancies exist for $X \leq 0.6$ only. In this range, some freeze-in occurs and consequently bound-hole effects could influence the results.

Table 3.6. Nonparabolic calculation of Y_{44} for Si at 77K.
 $d = 4.60$ eV.

μ (meV)	x_p	Y_{44}
-10.0	0.043	0.75
-5.0	0.083	1.45
0.0	0.16	2.62
3.0	0.23	3.6
6.0	0.32	4.8
11.0	0.53	7.3
15.5	0.79	9.9
21.5	1.25	13.8
30.0	2.15	19.7
40.0	3.6	26.2
50.0	5.3	32.
60.0	7.4	37.
70.0	9.8	41.
90.0	15.2	48.
125.0	26.7	58.
200.0	58.	76.
300.0	110.	94.

However, the predominant cause of deviations is rather the impurity-induced distortion of the band edge. As argued in Sec. 2.3, we believe that the data at high concentrations (μ around 100 meV) are representative of the theory with free holes in undistorted bands, and this is substantiated in Fig. 3.7.

Since Y_{44} is quadratic in d^2 , the fitted value of $d=4.6$ eV is well established. It should be compared with $d=(4.85\pm0.15)$ eV obtained by Laude et al. (1971) in a critical study of the indirect absorption edge in strained Si.

Following eq. (3-56) we can tentatively use a scaling to find a value for b . As shown in Table 3.2, Csavinszky and

Table 3.7. Nonparabolic calculation of Y_{44} for Si at 300K. $d = 4.60$ eV.

μ (meV)	X_p	Y_{44}
-50.0	0.35	2.08
-25.0	0.88	5.0
0.0	2.07	10.6
20.0	3.8	17.4
35.0	5.7	23.4
50.0	8.1	29.8
75.0	13.5	40.
125.0	28.5	57.
200.0	59.	75.
300.0	111.	94.

Table 3.8. Parabolic calculation of Y_{44} for Si at 77K. $d = 4.60$ eV.

$\mu/k_B T$	X_p	Y_{44}
-2.0	0.019	0.220
-1.0	0.048	0.52
0.0	0.112	1.08
1.0	0.230	1.83
2.0	0.41	2.61
4.0	0.80	3.6
8.0	2.53	5.6

Table 3.9. Experimental data on Y_{44} for Si at 77 and 300K. X_B is the boron concentration in units of 10^{19} cm^{-3} . Data for $X_B=0.25$ are from Mason and Bateman (1963), all others from Fjeldly et al. (1973).

X_B	0.22	0.25	0.6	1.5	2.6	7.0	16.
Y_{44} 77K		2.5	5.8		19.5	33.1	49.4
300K	0.9	0.9	2.3	7.4	12.2	26.6	45.3

Einspruch (1963) determined $Y_s=38$. for $X_B=11$. at $T=77\text{K}$. For this concentration we find $Y_{44}=43$. from Fig. 3.7, and so (3-56) yields

$$b \approx 4.60 \text{ eV} \left[\frac{1}{3} \cdot \frac{5.09}{7.96} \cdot \frac{0.76}{0.65} \cdot \frac{38.}{43.} \right]^{\frac{1}{2}}$$

$$= 2.16 \text{ eV} \quad (3-57)$$

which coincides with the result $b=(2.1 \pm 0.1) \text{ eV}$ found by Laude et al. (1971). This indicates that nonparabolicity may have the same effects on Y_s and Y_{44} .

Germanium

The input parameters are here $C_{44}=7.96 \cdot 10^{10} \text{ Nm}^{-2}$ ($C_s=4.03 \cdot 10^{10} \text{ Nm}^{-2}$) and $d = 4.40 \text{ eV}$. Tables 3.10 and 3.11 contain the theoretical results which are subsequently plotted in Fig. 3.8.

The experimental data of Beilin et al. (1970) give the temperature dependence of the elastic constants for "pure" Ge and for an acceptor doping of $9.9 \cdot 10^{19} \text{ cm}^{-3}$. However, there are two dubious features which render these data less reliable: (a) The elastic constants and their temperature variation for "pure" Ge disagree with the classical data by McSkimin (1953), and (b) the doping (Ga) changes also the bulk-modulus which is quite unlikely. Mean values in the range 77-300K are $Y_{44}=20$ and $Y_s=30$. Only one doped crystal was measured.

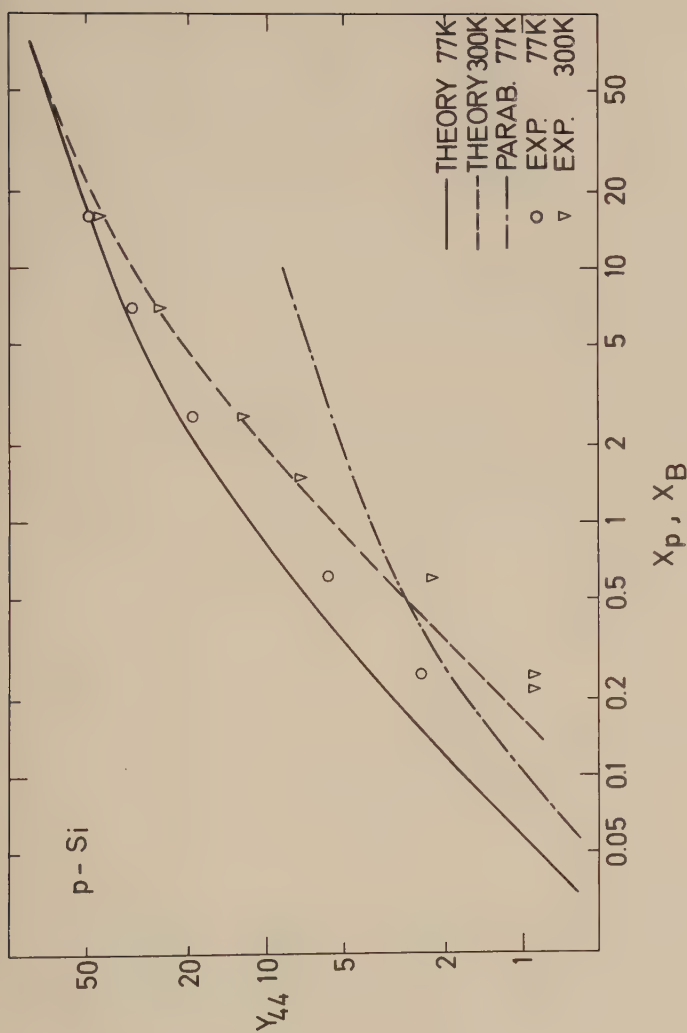


Figure 3.7. Theoretical and experimental results for Y_{44} in Si as function of hole or impurity concentration, X_p or X_B . The theory is fitted to experiment at the highest concentration, yielding $d=4.60$ eV.

Table 3.10. Nonparabolic calculation of Y_{44} for Ge at 77 and 300K. $d = 4.40$ eV.

μ (meV)	x_p (77)	Y_{44} (77)	x_p (300)	Y_{44} (300)
0.	0.06	0.47	0.49	1.65
20.	0.33	1.77	0.88	2.78
40.	0.88	3.4	1.47	4.3
75.	2.41	7.0	3.1	7.9
125.	5.9	14.1	6.7	14.5
200.	14.8	26.0	15.6	25.6
300.	33.	39.	34.	39.

Table 3.11. Parabolic calculation of Y_{44} for Ge at 77K. $d = 4.40$ eV.

μ/k_oT	x_p	Y_{44}
-1.0	0.023	0.183
0.0	0.054	0.38
1.0	0.111	0.64
2.0	0.20	0.91
3.0	0.32	1.15
6.0	0.80	1.70
9.0	1.45	2.09

Fig. 3.8 shows that the parabolic approximation is somewhat better than in Si, but actually rather bad in the range of concentrations relevant for the present type of investigation $x_p > 0.5$. The rise above $x_p = 1$ is due to the influence of the spin-orbit band. The agreement with experiment is perhaps surprising in view of the suspect quality of the latter. The value $d=4.40$ eV was chosen in accordance with the quantum cyclotron-resonance experiments under strain by Hensel and Suzuki (1974).

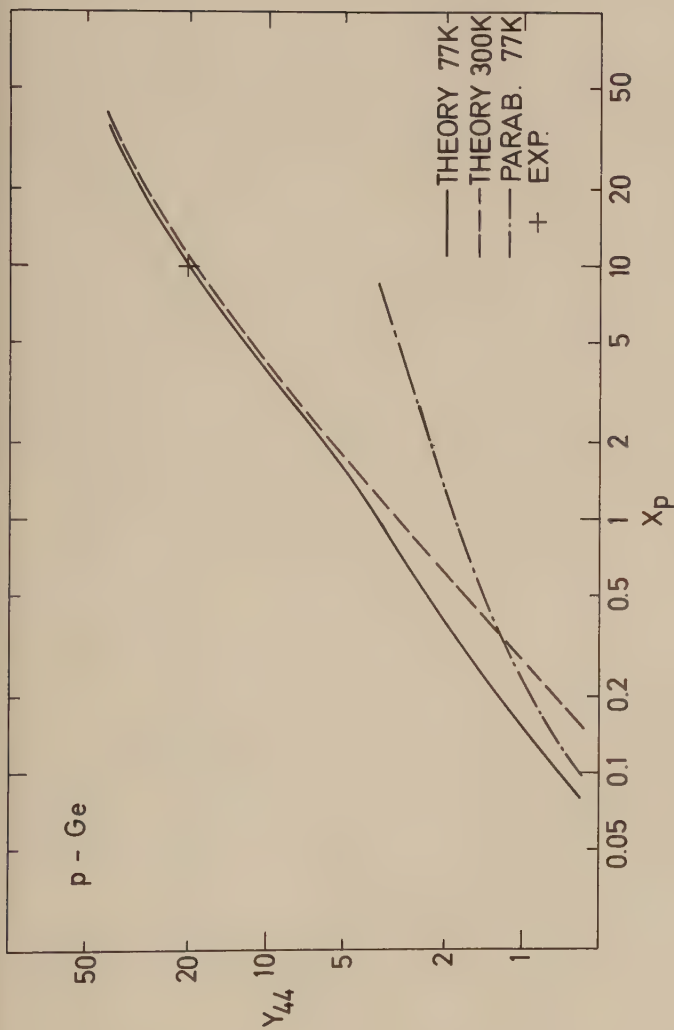


Figure 3.8. Theoretical results for Y_{44} in Ge as function of hole concentration, calculated for $\bar{d}=4.40$ eV. The cross marks the experimental datum discussed in the text.

The scaling according to eq. (3-56) yields the following result for b:

$$b \approx 4.40 \text{ eV} \cdot \left[\frac{1}{3} \cdot \frac{4.03}{6.71} \cdot \frac{0.51}{0.41} \cdot \frac{30}{20} \right]^{\frac{1}{2}} \quad (3-58)$$

$$= 2.70 \text{ eV}$$

which is considerably higher than $b = 2.20 \text{ eV}$ obtained by Hensel and Suzuki (1974). The disagreement is probably related to the dubious value of Y_S .

Gallium Arsenide

The input data are $C_{44} = 5.92 \cdot 10^{10} \text{ Nm}^{-2}$ ($C_S = 3.25 \cdot 10^{10} \text{ Nm}^{-2}$) and $d = 5.30 \text{ eV}$ is used. Results are listed in Tables 3.12 and 3.13, and the few experimental data in Table 3.14. This is all shown in Fig. 3.9.

Apart from scaling, the theoretical results are very similar to those for Ge. The agreement with experiment is acceptable for $X_p = 2.0$, but not very good for $X_p = 8.5$. We can offer no explanation for the inconsistency, but we should notice that the earlier mentioned experimental results for Si and Ge from this group are rather unreliable.

Table 3.12. Nonparabolic calculation of Y_{44} for GaAs at 77 and 300K. $d = 5.30 \text{ eV}$

$\mu (\text{meV})$	$X_p (77)$	$Y_{44} (77)$	$X_p (300)$	$Y_{44} (300)$
0.	0.09.	1.34	0.75	3.9
20.	0.56	4.7	1.33	6.3
40.	1.44	8.3	2.18	9.4
75.	3.7	15.1	4.3	16.0
125.	8.2	26.6	8.8	27.2
200.	17.6	47.	18.3	47.
300.	36.	73.	37.	72.

Table 3.13. Parabolic calculation of Y_{44} for GaAs at 77K.
 $d = 5.30$ eV.

$\mu/k_{\text{O}}T$	x_p	Y_{44}
-2.0	0.016	0.23
-1.0	0.040	0.55
0.0	0.093	1.13
1.0	0.191	1.92
2.0	0.34	2.74
3.0	0.54	3.5
6.0	1.39	5.1
9.0	2.50	6.3

Table 3.14. Experimental data for Y_{44} and Y_s is GaAs
obtained by Beilin et al. (1968).

X	2.0		8.5
T(K)	77	300	300
Y_s	11.	7.7	13.8
Y_{44}	12.	9.2	19.

The value $d = 5.30$ eV was chosen as an appropriate mean value of previous optical experiments: Dynamic piezoreflectance $d = (4.4 \pm 0.5)$ eV (Balslev 1967), piezoelectroreflectance $d = (6.5 \pm 0.3)$ eV (Pollak and Cardona 1968), piezoemission $d = (5.4 \pm 0.3)$ eV (Bhargava and Nathan 1967), and intervalence-band transitions $d = (5.3 \pm 0.4)$ eV (Balslev 1969). A cautious conclusion of the present work is that d could not be very different from 5.3 eV.

The scaling method (3.56) gives the following value for b :

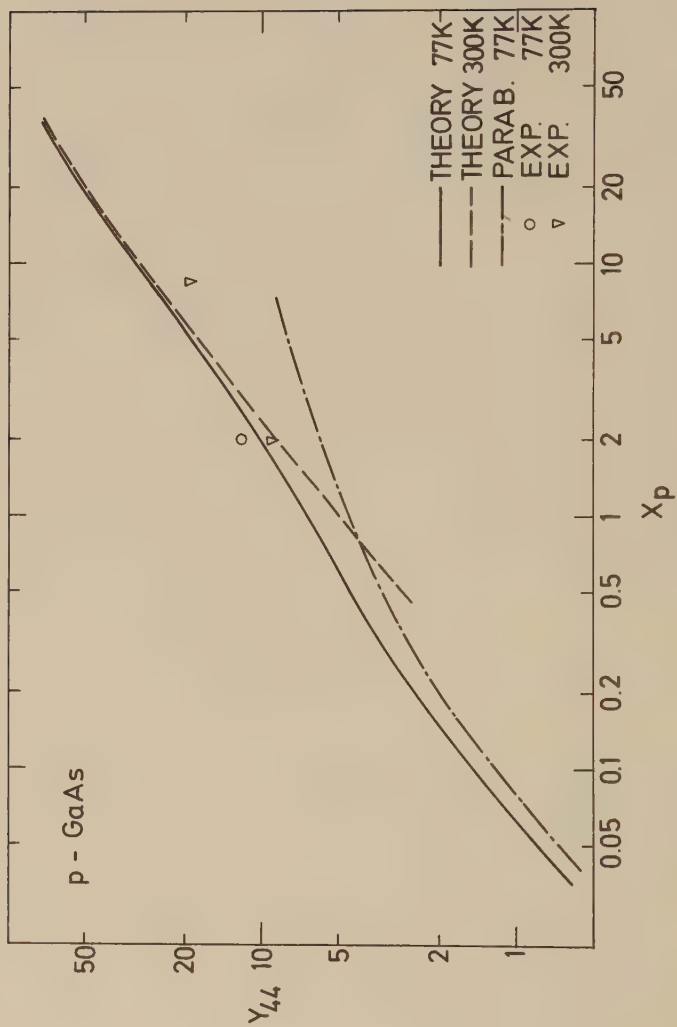


Figure 3.9. Theoretical and experimental results for Y_{44} in GaAs as function of hole or impurity concentration. $d = 5.30$ eV is used in the calculation.

$$b \approx 5.30 \text{ eV} \cdot \left[\frac{1}{3} \cdot \frac{3.25}{5.92} \cdot \frac{0.54}{0.47} \cdot \frac{7.7}{9.2} \right]^{\frac{1}{2}}$$

$$= 2.22 \text{ eV} \quad (3-59)$$

which is in agreement with results from the cited optical experiments.

Gallium Antimonide

The input data are $C_{44} = 4.32 \cdot 10^{10} \text{ Nm}^{-2}$ ($C_s = 2.4 \cdot 10^{10} \text{ Nm}^{-2}$) and $d = 4.60 \text{ eV}$. Calculated results are listed in Tables 3.15 and 3.16; and the experimental data obtained by Kuppenko et al. (1973) were given in Table 3.4. The results are all shown in Fig. 3.10.

The effects of nonparabolicity (and the split-off band) are surprisingly strong considering the relatively large spin-orbit splitting $\Delta_o = 770 \text{ meV}$. The theory is now in very good agreement with the experimental datum. A refined adjustment to experiment yields $d = 4.4 \text{ eV}$. Previous stress-optical measurements of d give: $d = 4.6 \text{ eV}$ (Guillaume and Lavallard 1970) and $d = (4.2 \pm 0.2) \text{ eV}$ (Pollak and Aggarwal 1971). Our result is thus satisfactory.

Table 3.15. Nonparabolic calculation of Y_{44} for GaSb at 77 and 300K. $d = 4.60 \text{ eV}$.

$\mu (\text{meV})$	$X_p (77)$	$Y_{44} (77)$	$X_p (300)$	$X_{44} (300)$
0.	0.07	0.86	0.55	2.14
20.	0.41	2.85	0.97	3.4
40.	1.06	4.7	1.59	5.0
75.	2.69	7.9	3.1	8.1
125.	5.9	12.9	6.3	13.2
200.	12.4	21.8	12.8	22.1
300.	24.2	36.	24.6	36.

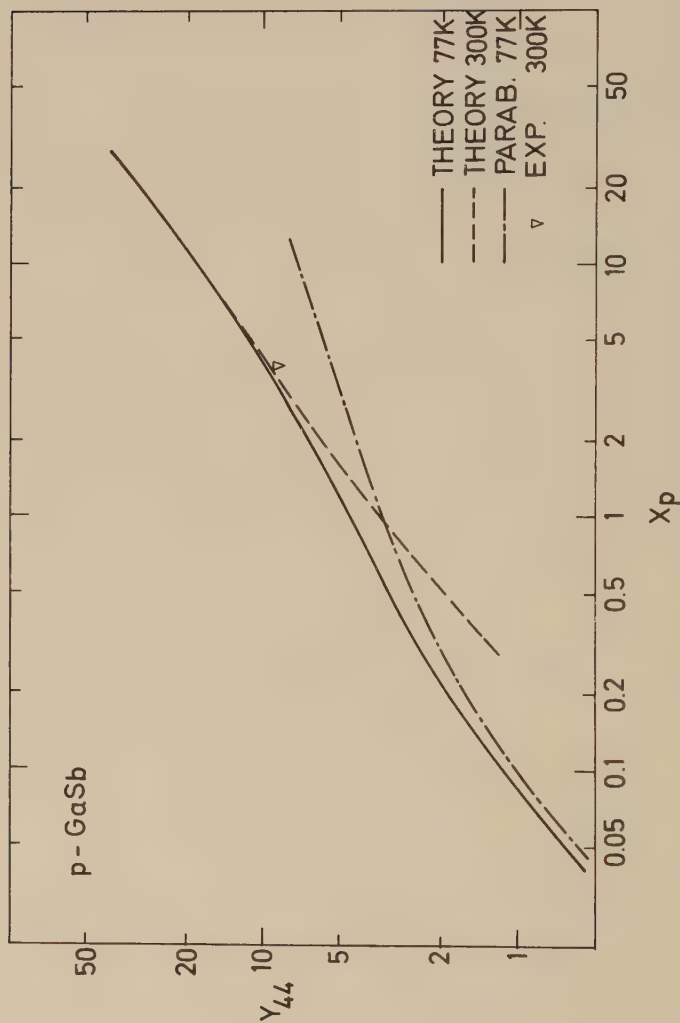


Figure 3.10. Theoretical and experimental results for Y_{44} in GaSb as function of hole or impurity concentration. $d = 4.60$ eV is used in the calculation.

Table 3.16. Parabolic calculation of Y_{44} for GaSb
at 77K. $d = 4.60$ eV.

$\mu/k_{\text{O}}T$	x_p	Y_{44}
-2.0	0.011	0.152
-1.0	0.029	0.36
0.0	0.067	0.74
1.0	0.137	1.26
2.0	0.246	1.80
3.0	0.39	2.28
6.0	1.00	3.4
9.0	1.79	4.1

The scaling (3-56) gives

$$b \approx 4.4 \text{ eV} \left[\frac{1}{3} \cdot \frac{2.40}{4.32} \cdot \frac{0.48}{0.40} \cdot \frac{14.8}{8.8} \right]^{\frac{1}{2}} \quad (3-60)$$

$$= 2.7 \text{ eV}$$

which is much larger than the 1.8-2.0 eV obtained in the above optical experiments. A result from a single experiment on one crystal should be treated with caution - and the validity of scaling has not been proved either.

Let us close this section by summing up the qualitative results. Our nonparabolic theory is not unique in the sense that the subject is treated in a paper by Kim et al. (1976) published after the completion of the present work. Their work was designed to cover the situation with a permanent strain too, and their formulas are not easily digested. Their results for Si at 77 and 300K are hampered by the use of obsolete valence-band parameters and somewhat arbitrary assumptions to repair this deficit. They claim only qualitative agreement, and they overlooked the effects of bound holes and impurity-induced band distortion. For Ge at 4.2K, their

results (for the same valence-band parameters) are in perfect agreement with ours. This is a valuable check.

Silicon is the only material for which extensive experimental data on γ_{44} exists, and it is therefore with regret that impurity effects are so pronounced for this material. For the other compounds studied, this problem should not be so severe since the critical impurity concentration, where the acceptor ionisation energy vanishes, is much lower there. The method of deriving acoustic deformation potentials from elastic-constant changes has been shown to give very accurate results when applied with caution, but more extensive experimental data are definitely needed for Ge, GaAs, and GaSb in addition to the materials for which no data exist at present.

One point has been left out: For the cases reported with sufficient documentation, the heavily-doped samples exhibit a change in the bulk modulus of the same relative order-of-magnitude as for the shear constants. The origin of this large change is unknown and has not been investigated.

The good agreement between theory and experiment for Si at the higher concentrations shows that it is worth while to proceed with the analysis of the analog behavior of the long-wavelength optical phonons.

4. INFLUENCE OF HOLES ON LONG-WAVELENGTH OPTIC PHONONS

The carrier-induced frequency change of ultrasonic waves has now been analysed on the basis of a free-energy argument. This is valid for frequencies much smaller than typical relaxation frequencies of holes. (We show in the present chapter that the condition is slightly different.) The renormalisation of high-energy phonons, on the other hand, is concerned with the phonon self-energy, the dynamic (and complex) change in the phonon energy following the quantum-mechanical coupling to the holes.

In Sec. 4.1 the self-energy concept is developed more or less from first principles by solution of a general Schrödinger equation for a reasonably simple case. The result is generalised to a real physical situation, where a photon is absorbed by emission of an optic phonon, and the phonon subsequently decays into secondary excitations, e.g. hole transitions in the valence bands. In real nonpolar semiconductors, the optic phonon is not created by photon absorption, but rather by Raman scattering. However, the formal theory is the same.

In the above situation, the absorption or Raman line has a Lorentzian form, but this does not correspond to reality. The phonon line overlaps the continuous spectrum due to optically (Raman) active hole intervalenceband excitations, and since the optic phonon is also coupled to these excitations, a more complicated spectrum results. This so-called Fano effect is analysed in detail in Sec. 4.2 based on the self-energy theory of the previous section. We believe that the present deduction is simpler than earlier theories, and it is also more general in the sense that further secondary decay modes are included. The existing interpretation of the Fano-type Raman spectrum of doped p-Si is then reconsidered in order to extract the extrinsic free-carrier effects properly. Data for Ge are also discussed.

The specific situation of long-wavelength optic-phonon self-energy is introduced in Sec. 4.3, and general formulas for

the hole-induced shift $\delta(\hbar\omega)$ and the broadening Γ are established. The formal relation to the free-energy result at low frequencies is discussed, and the direct connection to δC_{44} is elucidated.

Sec. 4.4 contains actual calculations of the shift and broadening for Si and Ge as function of free-hole concentration and temperature. Agreement with experimental data is rather good at high hole concentrations in Si and makes it possible to deduce a value for the optic deformation potential d_o . For Ge, the calculated broadening is an order of magnitude smaller than observed, and much work has gone into repairing this deficiency, and some unsuccessful attempts are discussed in this section.

The effect of the impurity distortion of the valence-band edge is proposed as the main reason for the discrepancy in Ge, and Sec. 4.5 contains a model calculation based on wave-vector smearing. Thus the $\bar{q}$ -dependence of the ideal self-energy is worked out approximately, and averaged values are compared with experiments. It is shown that agreement for Ge can be improved, and that the results for Si are little affected. This difference between the materials is due to different ratios of phonon energy to spin-orbit splitting. A reasonably reliable value of d_o can finally be inferred.

A short and incomplete account of the results for Si has been presented elsewhere (Lawaetz 1976).

4.1. General theory of self-energy

Ordinary time-independent perturbation theory tells us that the second-order correction to the energy E_o of a state $n=0$ is

$$\delta_o = \sum_{n \neq 0} \frac{|H_{n0}|^2}{E_o - E_n} \quad (4-1)$$

and that the life-time broadening is given by the golden rule

$$\Gamma_o = \pi \sum_{n \neq 0} |H_{no}|^2 \delta(E_o - E_n) \quad (4-2)$$

where H_{no} is the matrix element of the interaction Hamiltonian. Eqs. (4-1) and (4-2) are compounded into the formula

$$\delta_o - i\Gamma_o = \sum_{n \neq 0} \frac{|H_{no}|^2}{E_o - E_n + is} \quad (s \rightarrow 0_+) \quad (4-3)$$

Although this formula (properly modified by occupation factors) is actually very close to what is used in our calculations in Sec. 4.4, we have to establish that δ_o and Γ_o are the shift and broadening really observed in the phonon resonance experiment. At least for the Fano-type interference discussed in Sec. 4.2, it is not.

Let us consider the temporal evolution of the crystal system including electromagnetic waves and see how things happen when we excite one photon of energy E_o at time $t=0$. The model of interaction and decay is shown in Fig. 4.1. The

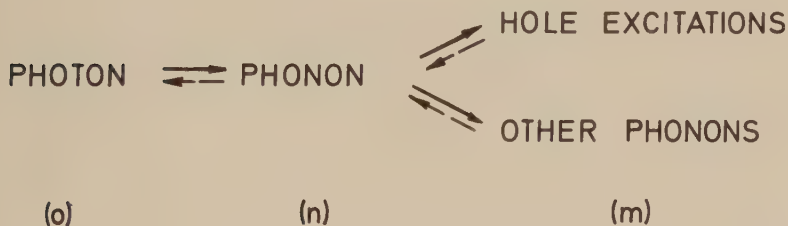


Figure 4.1. Temporal evolution of a crystal with one photon excited at $t=0$. "Other phonons" are excited by anharmonic effects. The letters below are state indices used in the theory.

Hamiltonian of the uncoupled system is H^0 and has the eigenvalues E_n and time-independent eigenfunctions ψ_n . Denoting the interaction Hamiltonian by H' , the Schrödinger equation is

$$i\hbar \frac{\partial \Psi}{\partial t} = H^0 \Psi + H' \Psi \quad (4-4)$$

We start the system in the state ψ_0 at time $t=0$, but this state decays due to the coupling, and it is this decay that we shall investigate.

We expand Ψ in the orthonormal system ψ_n

$$\Psi(t) = \sum_n b_n(t) \psi_n \quad (4-5)$$

and insert in (4-4):

$$i\hbar \dot{b}_n = E_n b_n + \sum_m H_{nm} b_m \quad (4-6)$$

where

$$H_{nm} = \int \psi_n^* H' \psi_m d\tau_r \quad (4-7)$$

(τ_r stands for the coordinates in ψ). Eq. (4-6) can be augmented by the initial condition $b_n(0_+) = \delta_{n0}$, and so

$$i\hbar \dot{b}_n = E_n b_n + \sum_m H_{nm} b_m + i\hbar \delta_{n0} \delta(t) \quad (4-8)$$

Introducing the Fourier transforms

$$b_n(t) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} dE G_n(E) \exp(-i\frac{t}{\hbar}E) \quad (4-9)$$

$$i\hbar \delta(t) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} dE \exp(-i\frac{t}{\hbar}E) \quad (4-10)$$

into (4-8), we find the following set of algebraic equations for the spectral function (or Green's function) $G_n(E)$:

$$(E-E_n)G_n(E) = \sum_m H_{nm}G_m(E) + \delta_{no} \quad (4-11)$$

Our procedure for solving this equation is adapted from Heitler (1954). We define the quantities $U_{no}(E)$ by

$$G_n(E) = U_{no}(E)G_o(E)\zeta(E-E_n) \quad (4-12)$$

(for $n \neq 0$) where

$$E\zeta(E) = 1, \quad \text{all } E \quad (4-13)$$

This is inserted in (4-11) for $n \neq 0$:

$$\begin{aligned} (E-E_n)U_{no}G_o\zeta(E-E_n) \\ = H_{no}G_o + \sum_{m \neq 0} H_{nm}U_{mo}G_o\zeta(E-E_m) \end{aligned} \quad (4-14)$$

or

$$U_{no}(E) = H_{no} + \sum_{m \neq 0} H_{nm}\zeta(E-E_m)U_{mo}(E) \quad (4-15)$$

We show presently that this equation is readily solved to any desired degree of accuracy. Once U_{no} has been found, we insert $G_{n \neq 0}$ from (4-12) in (4-11) to obtain G_o .

$$\begin{aligned} (E-E_o)G_o = 1 + H_{oo}G_o \\ + \sum_{n \neq 0} H_{on}\zeta(E-E_n)U_{no}G_o \end{aligned} \quad (4-16)$$

Taking $H_{oo} = 0$ for a properly chosen uncoupled system we find

$$G_o(E) = [E-E_o - z_o(E)]^{-1} \quad (4-17)$$

with

$$z_0(E) = \sum_{n \neq 0} H_{on} \zeta(E-E_n) U_{no}(E) \quad (4-18)$$

$z_0(E)$ is the self-energy of the state 0. We shall return to its physical significance shortly. Let us first present a simple solution U_{no} of eq. (4-15) in order to find an explicit expression for z_0 in (4-18).

If the photon state 0 is first generation, the phonon state n (on the left side of eq. (4-15)) is second generation, and m (on the right) is third. We assume no coupling between first and third generation, i.e. $H_{mo}=0$. The equation for U_{mo} is then

$$\begin{aligned} U_{mo}(E) &= H_{mn} \zeta(E-E_n) U_{no}(E) \\ &+ \sum_{m' \neq 0, n} H_{mm'} \zeta(E-E_{m'}) U_{m'o}(E) \end{aligned} \quad (4-19)$$

The fourth generation terms m' are neglected in this iterative procedure. The rest is inserted in (4-15):

$$U_{no} = H_{no} + \sum_{m \neq 0} H_{nm} \zeta(E-E_m) H_{mn} \zeta(E-E_n) U_{no} \quad (4-20)$$

or with the abbreviation ($n \neq 0$)

$$z_n(E) = \sum_{m \neq 0} H_{nm} \zeta(E-E_m) H_{mn} \quad (4-21)$$

$$(1 - z_n(E) \zeta(E-E_n)) U_{no}(E) = H_{no} \quad (4-22)$$

Here we multiply by $(E-E_n)$ and use (4-13)

$$U_{no}(E) = \frac{E-E_n}{E-E_n - z_n(E)} H_{no} \quad (4-23)$$

Final substitution into (4-18) yields

$$z_0(E) = \sum_{n \neq 0} \frac{H_{on} H_{no}}{E-E_n - z_n(E)} \quad (4-24)$$

If the decay processes are so that there is a one-to-one correspondence between decaying state and decay product (no alternative paths), further iterations would lead to z_n having the same form as z_0 . Other situations will be touched on later.

With $G_0(E)$ of the form (4-17) we find from the definition (4-9)

$$b_0(t) = -\frac{1}{2\pi i} \int_{-\infty}^{\infty} dE (E - E_0 - z_0(E))^{-1} \exp(-i\frac{t}{\hbar}E) \quad (4-25)$$

The pole in the integrand is close to $E = E_0 + z_0(E_0)$, and the integral will be approximated by taking $z_0(E) \approx z_0(E_0)$. Since

$$z(E) = \lim_{s \rightarrow 0_+} (E + is)^{-1} \quad (4-26)$$

eq. (4-21) yields $\text{Im} z_n < 0$, and so from (4-24) $\text{Im} z_0 < 0$. The pole in (4-25) is thus below the real axis, and complex integration around this half-plane then gives

$$b_0(t > 0) = \exp[-i\frac{t}{\hbar}(E_0 + z_0(E_0))] \quad (4-27)$$

$$b_0(t < 0) = 0 \quad (4-28)$$

The physical significance of $z_0(E_0)$ follows: $\text{Re} z_0(E_0)$ stands for the shift in the resonance energy E_0 , and $-\text{Im} z_0(E_0)$ is related to the decay rate

$$|b_0|^{-2} \frac{d}{dt} |b_0(t)|^2 = \tau^{-1} = -\frac{2}{\hbar} \text{Im} z_0(E_0) \quad (4-29)$$

A similar interpretation holds for z_n .

In the real situation we use the photon as a probe and control its energy $E = E_0 + \text{Re} z_0(E_0)$. The photon absorption probability is then proportional to

$$-\text{Im} z_0(E) = -\text{Im} \sum_{n \neq 0} \frac{H_{on} H_{no}}{E - E_n - z_n(E)} \quad (4-30)$$

This function of the energy E is essentially the absorption spectrum. ($\text{Re}z_0(E)$ is related to the polarisation spectrum). It follows from (4-30) that $\text{Re}z_n(E)$ and $-\text{Im}z_n(E)$ are the shift resp. lifetime-broadening of the states n , however, with energy E rather than E_n .

One further modification is needed. The self-energy of a particular excitation (photon, phonon, electron-hole pair) is really the difference between absorption self-energy of the final state and emission self-energy of the initial state. We should also add the corresponding emission/absorption processes. The total self-energy is consequently (for all n)

$$\tilde{z}_n(E) = \left[z_n^{N+1}(E) + z_n^{N+1}(-E) \right] - \left[z_n^N(-E) + z_n^N(E) \right] \quad (4-31)$$

where the superscript indicates the number of photons or phonons in the state. Since the squared matrix elements are linear functions of particle number, (4-31) is equivalent to

$$\tilde{z}_n(E) = z_n^1(E) + z_n^0(-E) \quad (4-32)$$

The previous analysis assumed $E(=E_0) > 0$, and so $z_n(-E)$ corresponding to emission processes is not yet defined. Reconsideration of the previous analysis shows that the result analogous to (4-24) is

$$z_0(-E) = \sum_{n \neq 0} \frac{|H_{n0}|^2}{-E - E_n - z_n^*(E)} \quad (4-33)$$

The self-consistent expression for the general, combined self-energy (4-32) is then

$$\begin{aligned} \tilde{z}_n(E) = \sum_{m \neq n} |H_{mn}|^2 \left\{ (E - E_m - \tilde{z}_m(E))^{-1} \right. \\ \left. + (-E - E_m - \tilde{z}_m^*(E))^{-1} \right\}, \quad E > 0 \end{aligned} \quad (4-34a)$$

$$\tilde{z}_n(E) = \tilde{z}_n^*(-E), \quad E < 0 \quad (4-34b)$$

The self-energy defined in this way is an analytical function for all complex E , a feature related to the reality of its physical interpretation. From the Cauchy integral theorem we can then derive the Kramers-Kronig relations between real and imaginary parts, but we have no use for that here.

In most cases there is practically no difference between the Lorentz-form (4-30) and the Drude-Lorentz-form (4-34) because the second term in (4-34a) is nonresonant. The main importance of (4-34) shows up when E , E_m , and $-\text{Im}z_n$ are of the same order of magnitude as in the case of free particles where the spectrum of excitation energies extends down to zero.

A typical Lorentzian shape like (4-30) is sketched in Fig. 4.2 showing the significance of the spectrum parameters

$$\delta_n = \text{Re}z_n \quad (4-35)$$

$$\Gamma_n = -\text{Im}z_n$$

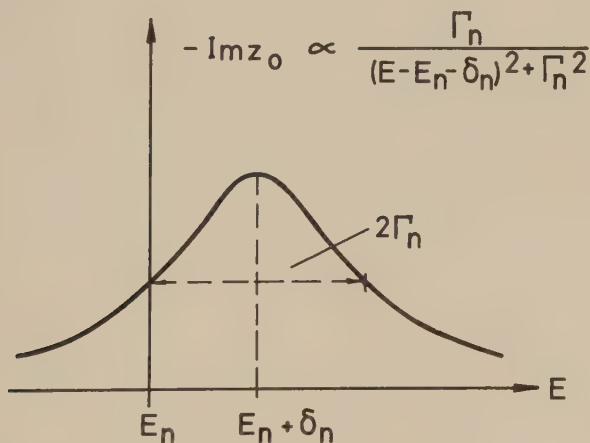


Figure 4.2. Typical Lorentzian with constant broadening Γ_n and resonance energy shift δ_n away from the bare resonance E_n .

We have taken z_n to be independent of energy E which is relevant for the situation when state n decays into a featureless "background" continuum (e.g. optic phonon decay into hole excitations in the valence band). If the background spectrum has significant structure, eq. (4-30) shows that this structure can be reflected in $-\text{Im}z_0$. This is a generalised case of side-bands.

We have here been concentrating on absorption and emission whereas the optic phonon is excited in a Raman scattering experiment. The only formal difference is that our energy E should be zero at the laser excitation energy.

4.2 The Fano effect

The nonpolar optic phonon is Raman active, but so are also the hole excitations. The interaction picture in Fig. 4.1 should therefore be modified as shown in Fig. 4.3 which have interaction between two types of second-generation excitations. This coupling between a discrete excitation (phonon) and a continuum (hole excitations) leads to interference which distorts the Lorentzian resonance considerably. This is called the Fano effect (Fano 1961) and has recently been analysed for the case of Raman scattering by Balkanski et al. (1975) and Bechstedt and Peuker (1975). Cerdeira et al. (1973) applied Fano's formulas to the present experimental situation, the first such case in connection with Raman scattering.

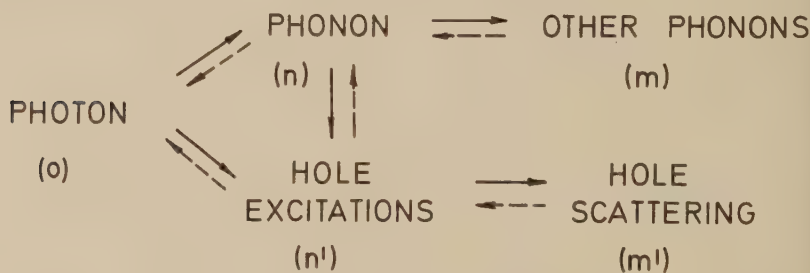


Figure 4.3. Decay scheme of an initial phonon with interacting second-generation excitations. The letters are used to indicate the states of the various categories.

The most general theory so far (Bechstedt and Peuker 1975) gives the following result for the ratio of the total intensity I_t to the continuum (background) intensity I_c :

$$\frac{I_t}{I_c} = \frac{|\tilde{q} + \epsilon|^2}{1 + \epsilon^2} \quad (4-36)$$

where

$$\epsilon = \frac{E - E_n - \delta_n}{\Gamma_n} \quad (4-37)$$

and $\tilde{q}$ is a certain complex coupling ratio, which we shall define later. Earlier theories assumed $\tilde{q}$ to be real, and all have neglected third-generation states so that δ_n and Γ_n are the shift and broadening of the optic phonon due to hole excitations when the interaction between photon and holes is zero. However, the intrinsic broadening of the phonon due to anharmonic effects is comparable to the extrinsic hole-induced effects Γ_n , and so the existing theory is inadequate. Furthermore, we have to reconsider the interpretation of the experimental data in the light of a complex $\tilde{q}$. The present development is rather straightforward after the establishment of the basis in the previous section.

From eqs. (4-18), (4-15), and (4-19) we have the following extensions, noting that n is a single excitation:

$$z_o(E) = H_{on} \zeta(E-E_n) U_{no} + \sum_{n'} H_{on'} \zeta(E-E_{n'}) U_{n'o} \quad (4-38)$$

$$U_{no} = H_{no} + \sum_m H_{nm} \zeta(E-E_m) U_{mo} + \sum_{n'} H_{nn'} \zeta(E-E_{n'}) U_{n'o} \quad (4-39)$$

$$U_{n'o} = H_{n'o} + \sum_{m'} H_{n'm'} \zeta(E-E_{m'}) U_{m'o} + H_{n'n} \zeta(E-E_n) U_{no} \quad (4-40)$$

$$U_{mo} = H_{mn} \zeta(E-E_n) U_{no} \quad (4-41)$$

$$U_{m'o} = H_{m'n} \zeta(E-E_n) U_{n'o} \quad (4-42)$$

Introducing the secondary partial self-energies

$$z_n' = \sum_m H_{nm} \zeta(E-E_m) H_{mn} \quad (4-43)$$

$$z_{n'}' = \sum_{m'} H_{n'm'} \zeta(E-E_{m'}) H_{m'n'} \quad (4-44)$$

eqs. (4-38)-(4-42) can be solved exactly to give

$$\begin{aligned} z_o(E) &= \frac{H_{on} H_{no}}{E-E_n-z_n} + \sum_{n'} \frac{H_{on'} H_{n'o}}{E-E_{n'}-z_{n'}'} \\ &+ \sum_{n'} \frac{2\text{Re}\{H_{on} H_{nn'} H_{n'o}\}}{(E-E_n-z_n)(E-E_{n'}-z_{n'}')} \\ &+ \sum_{n'n''} \frac{H_{on'} H_{n'n''} H_{nn''} H_{n''o}}{(E-E_{n'}-z_{n'}')(E-E_n-z_n)(E-E_{n''}-z_{n''}')} \end{aligned} \quad (4-45)$$

where the self-energy of the continuum states is denoted by $z_{n'}$ since details are unimportant, and z_n is the total self-energy of the phonon state n :

$$z_n(E) = z_n' + \sum_{n'} \frac{H_{nn'} H_{n'n}}{E-E_{n'}-z_{n'}'} \quad (4-46)$$

Let the density-of-states in the continuum be a constant ρ_2 . z_n is then independent of E :

$$E_n + z_n = E_1 - i\Gamma_1 \quad (4-47)$$

so that E_1 includes the shift $\text{Re} z_n$. Further, we take the matrix elements to be constant

$$H_{no} = H_{10}, \quad H_{n'o} = H_{20}, \quad H_{nn'} = H_{12} \quad (4-48)$$

In this way,

$$\Gamma_1 = \Gamma_1' + \rho_2 |H_{12}|^2 \quad (4-49)$$

as derived from (4-46) and (4-47). Finally, we define the complex quantity

$$\tilde{q} = \frac{H_{10}}{\rho_2 H_{12} H_{20}} \quad (4-50)$$

The absorption (or scattering intensity) is then

$$\begin{aligned} -\text{Im}z_o(E) = & \frac{|H_{10}|^2 \Gamma_1}{(E-E_1)^2 + \Gamma_1^2} + \rho_2 |H_{20}|^2 \\ & + 2\text{Re}\{H_{01}H_{12}H_{20}\} \rho_2 \frac{E - E_1}{(E-E_1)^2 + \Gamma_1^2} \\ & - \rho_2^2 |H_{20}|^2 |H_{12}|^2 \frac{\Gamma_1}{(E-E_1)^2 + \Gamma_1^2} \end{aligned} \quad (4-51)$$

$$\frac{I_t}{I_c} = \frac{-\text{Im}z_o(E)}{\rho_2 |H_{20}|^2} = 1 + \frac{\Gamma_1 - \Gamma_1'}{\Gamma_1} \cdot \frac{|\tilde{q}|^2 - 1 + 2\epsilon \text{Re}\tilde{q}}{1 + \epsilon^2} \quad (4-52)$$

with

$$\epsilon = \frac{E - E_1}{\Gamma_1} \quad (4-53)$$

For $\Gamma_1' = 0$ (no intrinsic phonon broadening) eq. (4-52) is identical to (4-36), the result derived by Bechstedt and Peuker (1975). In fact, (4-52) could have been obtained from (4-36) by convolution with a Lorentzian with shift δ_1' and broadening Γ_1' in the usual way:

$$I_t(E) = \int_{-\infty}^{\infty} dE' I_t^o(E') \frac{\Gamma_1'/\pi}{(E-E'-\delta_1')^2 + \Gamma_1'^2} \quad (4-54)$$

The original interpretation of experimental data by Cerdeira et al. (1973) used $\Gamma_1' = 0$ and took $\tilde{q}$ to be real. How should

this interpretation be modified for the general case? A careful inspection of their fitting procedure shows that the observed intensity I_t is normalised additively to the minimum intensity I_{tm} (which is zero in the simple model) and subsequently multiplicatively normalised to unity for the asymptotic $|\epsilon| \rightarrow \infty$ intensity $I_{t\infty} - I_{tm}$. From (4-52) we find for this observed intensity function:

$$F_q(\epsilon) = \frac{I_t - I_{tm}}{I_{t\infty} - I_{tm}} = 1 + \frac{q^2 - 1 + 2q\epsilon}{1 + \epsilon^2} \quad (4-55)$$

where the new quantity q is related to the complex $\tilde{q}$ by

$$q = \{ |\tilde{q}|^2 - 1 + [(|\tilde{q}|^2 - 1)^2 + 4(\text{Re}\tilde{q})^2]^{\frac{1}{2}} \} / 2\text{Re}\tilde{q} \quad (4-56)$$

This holds for $\text{Re}\tilde{q} \neq 0$. In the special case $\text{Re}\tilde{q} = 0$, there is no minimum and (4-52) is a simple Lorentzian superimposed on the continuum intensity. The same is obtained from (4-55) for $|q| \gg 1$. The Fano-type line shape (4-55) is shown in Fig. 4.4.

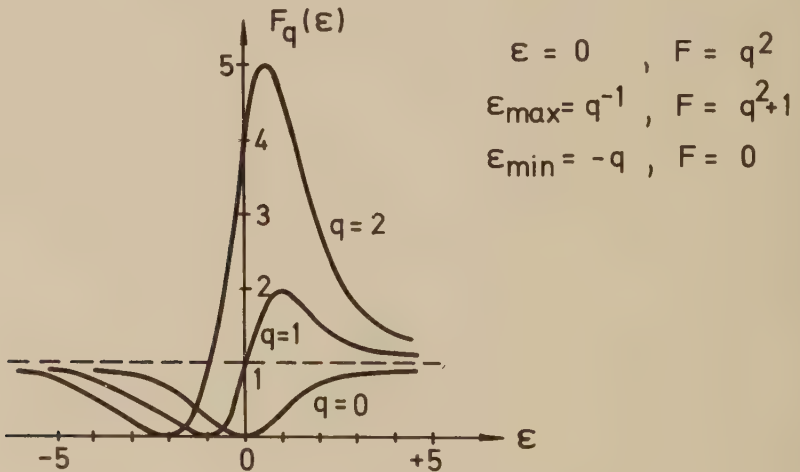


Figure 4.4. The Fano line-shape function $F_q(\epsilon)$ for a few values of $q \geq 0$. For $q < 0$ we have $F_q(\epsilon) = F_{-q}(-\epsilon)$.

We conclude from this analysis that the parameters originally extracted from experiment (Cerdeira et al. 1973), i.e. broadening and shift, should be interpreted as the total broadening and shift of the phonon resonance. Also the value of q has a different background, and the unsystematic behavior observed for $q < 1$ may be an indication that q has a small nonzero imaginary component.

In the following, we have collected and corrected the experimental data so that the end products are the hole-induced shifts and broadenings for specified hole concentrations. (Actually, the hole concentrations are rather acceptor concentrations).

The most accurate data are from the Fano line-shape analyses for p-Si (Cerdeira et al. 1973). The observed broadening Γ_{obs} should here be transformed into extrinsic broadening Γ by subtraction of the intrinsic broadening Γ_i determined by Hart et al. (1970):

$$\begin{aligned} T = 0-77\text{K}: \Gamma_i &= 1.0 \text{ cm}^{-1}, \frac{\Gamma_i}{\hbar\omega} = 1.9 \cdot 10^{-3} \\ T = 300\text{K}: \Gamma_i &= 2.0 \text{ cm}^{-1}, \frac{\Gamma_i}{\hbar\omega} = 3.8 \cdot 10^{-3} \end{aligned} \quad (4-57)$$

The corresponding shifts are the extrinsic shifts directly (already corrected). In convenient units

$$\begin{aligned} X &= \frac{P}{10^{-19} \text{ cm}^{-3}} \\ Y &= - \frac{\delta(\hbar\omega)}{\hbar\omega} \cdot 10^3 \\ Z &= \frac{\Gamma}{\hbar\omega} \cdot 10^3 \end{aligned} \quad (4-58)$$

This is listed in Tables 4.1 and 4.2.

One interesting feature of the data as shown in the tables is the independence of the product qZ on carrier concentration

Table 4.1. Extrinsic shifts Y and broadenings Z of the optic phonon in p-Si at $T=77K$. The data are from Cerdeira et al. (1973). The values of q are given for the laser wavelength 4880 Å.

X	$q(4880)$	Y	Z_{obs}	Z	qZ
0.6	32.8	0.2	2.2	0.3	10
1.7	12.4	0.8	5.3	3.4	43
2.6	14.6	0.1 ^{*)}	6.1	4.2	61
4.0	9.8	2.2	8.4	6.5	63
7.0	4.7	3.5	11.5	9.6	45
16.	3.7	12.6	15.4	13.5	50
40.	2.8	28.0	20.2	18.3	51

^{*)} Rather $|Y| < 0.1$

Table 4.2. Extrinsic shifts Y and broadenings Z of the optic phonon in p-Si at $T=300K$. The data are from Cerdeira et al. (1973). The values of q are given for the laser wavelength 4880 Å.

X	$q(4880)$	Y	Z_{obs}	Z	qZ
7.	8.8	3.8	10.7	6.9	60
16.	5.1	9.3	15.6	11.8	60
40.	3.2	22.7	21.8	18.2	58

and temperature. This can be understood from the basic theory. The free-hole Raman intensity $\rho_2 |H_{20}|^2$ contains (in the effective ρ_2) exactly the same occupation factors as $\Gamma = \rho_2 |H_{12}|^2$ since it involves a sum over the same occupied hole states. Provided that the matrix elements $|H_{20}|^2$ and $|H_{12}|^2$ do not vary in a drastically different way with

holek vector, which is more or less assumed in the theory leading to (4-52) and which is quite reasonable, the definition of q in (4-50) shows that $|\tilde{q}|^2 \Gamma^2$ is independent of the carrier distribution. For $|\text{Re}\tilde{q}| \gg |\text{Im}\tilde{q}|$, we then get $qZ = \text{cst.}$ as observed. We conclude that the above condition is generally satisfied. An exception occurs for low concentrations at 77K, and we interpret this as due to impurity-induced distortion. Cerdeira et al. (1973) argued erroneously that $q^2 \Gamma^3$ should be constant, and their experimental verification of $(q^2 \Gamma_{\text{obs}}^3)^{1/5} \approx \text{cst.}$ is not relevant, since Γ_{obs} is not the same as Γ , and taking the 1/5 power makes almost any decent function look like a constant.

An older set of data on p-Si is presented by Cerdeira and Cardona (1972). At that time the relevance of the Fano-type line shape had not been realised and so the data were fitted by Lorentzian-like spectra. The actual interpretation is not well documented in the paper. In particular, no unique extraction of broadening values is possible from the given information. We have therefore concentrated on the resonance shift and assume $\delta(\hbar\omega)_{\text{obs}}$ to be the peak shift. From eq. (4-55) we then find

$$\delta(\hbar\omega)_{\text{obs}} = \delta(\hbar\omega)_{\text{actual}} + q^{-1} \Gamma_{\text{total}} \quad (4-59)$$

or

$$Y = Y_{\text{obs}} + q^{-1} (Z + Z_{\text{intrinsic}}) \quad (4-60)$$

In the original paper (Cerdeira and Cardona 1972) Y_{obs} is shown in a diagram which we have translated into the numbers in Tables 4.3 and 4.4. The data are then processed according to (4-60) using interpolated q values from Tables 4.1 and 4.2 combined with Z derived from $qZ \approx 60$ and $Z_{\text{intrinsic}}$ from (4-57). This procedure is reasonable because the second term in (4-60) is a correction. The deduced values of the extrinsic shift will be compared with theoretical results in Sec. 4.4.

Table 4.3. Extrinsic shifts γ of the optic phonon in p-Si at 77K. The data γ_{obs} are derived from Cerdeira and Cardona (1972).

X	q(4880)	γ_{obs}	Z	$q^{-1}(Z+Z_{\text{intr}})$	γ
1.0	25	0.4 ^{*)}	2.4	0.2	0.6
5.9	6.6	1.8	9.1	1.7	3.5
6.6	5.4	1.7	11.1	2.4	4.1
10.0	4.4	5.6	13.6	3.5	9.1
12.3	4.1	6.0	14.6	4.0	10.0
14.0	3.9	6.0	15.3	4.4	10.4

^{*)} Very uncertain: $0 < \gamma_{\text{obs}} \leq 0.4$.

Table 4.4. Extrinsic shifts γ of the optic phonon in p-Si at 300K. The data γ_{obs} are derived from Cerdeira and Cardona (1972).

X	q(4880)	γ_{obs}	Z	$q^{-1}(Z+Z_{\text{intr.}})$	γ
1.0	50	0.6	1.2	0.1	0.7
2.0	35	1.2	1.7	0.2	1.4
3.0	20	2.0	3.0	0.3	2.3
5.9	10	2.8	6.0	1.0	3.8
6.6	9.2	3.4	6.5	1.1	4.5
10.0	6.8	5.5	8.8	1.9	7.4
12.3	6.0	6.0	10.0	2.3	8.3
14.0	5.5	6.0	10.9	2.7	8.7

The paper by Cerdeira and Cardona (1972) also gives results for p-Ge at various degrees of doping. A notable feature of the spectra is the presence of asymmetry of the Fano-type with negative q at intermediate concentrations ($X \leq 2$), but symmetric Lorentzian shapes at higher concentrations. The broadening increases monotonically with concentration.

The negative value of q reflects $\text{Re}\tilde{q} < 0$, and we can explain why the signs are different for Ge and Si. The matrix element H_{20} of the indirect hole-excitation process contains $(E_g - E_L)$ in the denominator, where E_g is the lowest optically active direct band gap at $k=0$ and E_L is the laser photon energy. The experiments used $\lambda_L = 4880 \text{ \AA}$ corresponding to $E_L = 2.5 \text{ eV}$. For Si $E_g = 3.3 \text{ eV}$ (E'_O) and for Ge $E_g = 0.9 \text{ eV}$ (E_O). It follows that H_{20} and so $\text{Re}\tilde{q}$ has opposite sign in the two materials.

The curious point is that $|q|$ obviously goes through a minimum at intermediate X , and consequently $|q|\Gamma_{\text{obs}}$ is not independent of X . (Γ_{obs} is the observed extrinsic broadening). This disagrees with the theory and its experimental verification for Si and is the first indication of the anomalous behavior of Ge. As we shall see in Sec. 4.4, the theoretical values of Γ are an order of magnitude smaller than Γ_{obs} . Furthermore, Γ_{theor} exhibits a maximum at intermediate X , and so qualitatively $|q|\Gamma_{\text{theor}}$ is nearly independent of X as in the ideal theory.

Table 4.5 shows the extrinsic values of $\delta(\hbar\omega)$ and Γ as obtained by Cerdeira and Cardona (1972) without corrections for finite $|q|$, because q is not known. Such corrections to Y are negative due to $q < 0$ and could be quite appreciable for $X \sim 1$. (The intrinsic Z is 2.7 at 77K and 6.7 at 300K). We conclude that the high concentration data are the most reliable representatives of the real situation.

4.3 Phonon self-energy

By the Raman scattering process we excite an optic phonon with a wave vector $\bar{q}$ which for all practical purposes can be taken to be zero. The hole transitions contributing to the phonon self-energy are thus all possible vertical inter-valence-band transitions from occupied to unoccupied states. According to eq. (4-34) the phonon self-energy $z_p(E)$ is then

Table 4.5. Extrinsic shifts Y and broadenings Z for the optic phonon in p-Ge. The data are derived from Cerdeira and Cardona (1972). T = 77 and 300K.

X	Y (77)	Z (77)	Y (300)	Z (300)
0.58	—*)	—	1.4	1.4
1.0	—*)	—	1.9	1.4
2.0	1.9	3.2	3.4	4.2
19.	14.	8.5	14.	8.2
24.	17.	11.6	19.	9.5

*) The values shown in the reference paper could not possibly have been detected because of instrumental broadening.

$$\begin{aligned} \tilde{Z}_P(E) = 2 \sum_{\lambda \vec{k}} \sum_{\lambda' \neq \lambda} f(E_{\lambda}) \left[1 - f(E_{\lambda'}) \right] |H_{\lambda\lambda'}^O(\vec{k})|^2 \\ \times \left\{ \left[E + E_{\lambda} - E_{\lambda'}, +is \right]^{-1} + \left[-E + E_{\lambda} - E_{\lambda'}, -is \right]^{-1} \right\} \end{aligned} \quad (4-61)$$

where λ is the band index, E_{λ} and $E_{\lambda'}$ are taken at the same $\vec{k}$ vector, the squared matrix element is given by (B-19)

$$|H_{\lambda\lambda'}^O(\vec{k})|^2 = \frac{\hbar d_O^2}{2\rho\omega a_c} g_{\lambda\lambda'}(\vec{k}) \quad (4-62)$$

and s is a vanishingly small quantity having the sign of E . Since the hole excitation energies $(E_{\lambda}, -E_{\lambda'})$ constitute an almost structureless continuum, the shift and width of these states are irrelevant and can be replaced by s . We shall return to a critical examination of this feature at the end of the next section.

In eq. (4-61), the factor $\{ \}$ is antisymmetric with respect to an interchange of λ and λ' . The expression can therefore be reduced to either of the following two:

$$\tilde{z}_p(E) = 2 \sum_{\lambda \vec{k}} \sum_{\lambda' \neq \lambda} f(E_{\lambda}) |H_{\lambda\lambda'}^0(\vec{k})|^2$$

$$\times \left\{ \left[E + E_{\lambda} - E_{\lambda'} + i\epsilon \right]^{-1} + \left[-E + E_{\lambda} - E_{\lambda'} - i\epsilon \right]^{-1} \right\} \quad (4-63)$$

$$= 2 \sum_{\lambda \vec{k}} \sum_{\lambda' \neq \lambda} |H_{\lambda\lambda'}^0(\vec{k})|^2 \frac{f(E_{\lambda}) - f(E_{\lambda'})}{E + E_{\lambda} - E_{\lambda'} + i\epsilon} \quad (4-64)$$

The latter is the expression normally seen for self-energy or polarisation, whereas the former is used in the present work.

The rest of this section will be devoted to a qualitative understanding of the behavior of $\tilde{z}_p$, i.e. its frequency, concentration, and temperature dependence, and of the relation of $\tilde{z}_p$ to the free-energy theory of Chapter 3 at very low frequencies.

For a simple model with isotropic heavy and light holes at $T = 0$ K as shown in Fig. 4.5, the energy (or frequency) dependence of $\tilde{z}_p$ is shown in Fig. 4.6. Smearing of the sharp curves are caused by $k_B T > 0$ and the actual anisotropy of the hole bands (as in Ge), and this is illustrated in Fig. 4.7. For Si, the inclusion of the spin-orbit split-off band results in a modification of the structure, but the positive and negative regions of $\text{Re} \tilde{z}_p(E)$ at high, respectively low

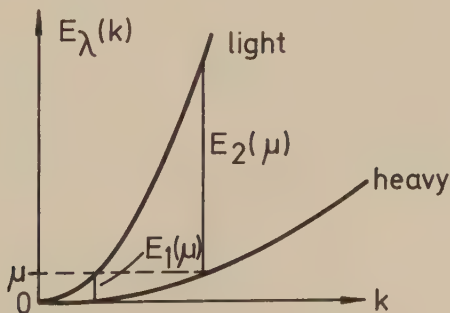


Figure 4.5. Simple isotropic band structure with light and heavy holes. At $T=0$ all states from 0 to μ are occupied.

energies are general features.

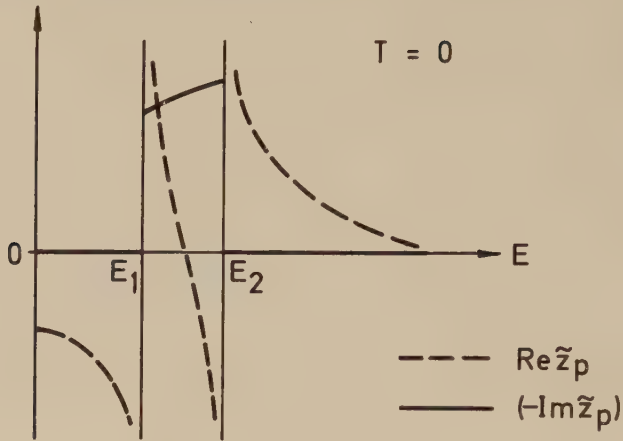


Figure 4.6. Energy dependence of $\tilde{\epsilon}_p$ at $T=0$ for the isotropic band structure in Fig. 4.5.

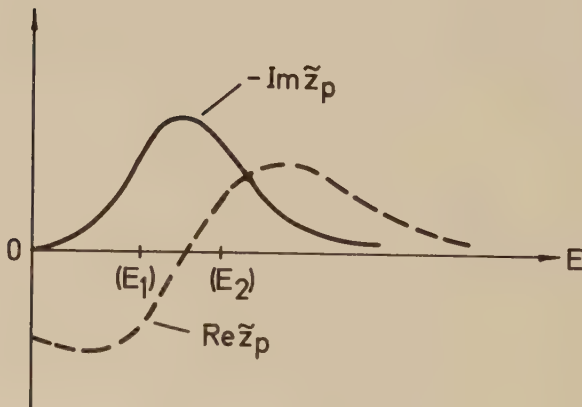


Figure 4.7. Energy dependence of $\tilde{\epsilon}_p$ at $T>0$ for an anisotropic band structure similar to Fig. 4.5. The horizontal position of the structures depends on the carrier concentration through the chemical potential μ .

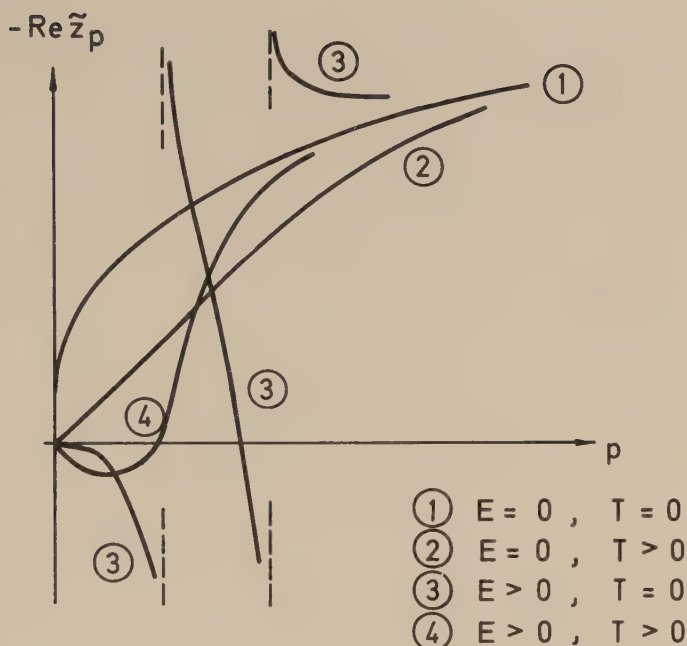


Figure 4.8. Typical variation of $\text{Re} \tilde{z}_p$ with hole concentration p . Curves ① and ② are similar to the behavior of the elastic-constant changes, cf. Fig. 3.1.

For a fixed observation energy E (essentially the phonon energy), the diagrams can be inverted to give the dependence on hole concentration. In the case of $\text{Re} \tilde{z}_p$, typical examples are shown in Fig. 4.8.

The equation (4-63) for $\tilde{z}_p(E)$ contains no singularity for $E > 0$, and so in this limit we have

$$\text{Re} \tilde{z}_p(0) = 4 \sum_{\lambda \bar{k}} f(E_\lambda) \sum_{\lambda' \neq \lambda} \frac{|H_{\lambda \lambda'}^0(\bar{k})|^2}{E_\lambda - E_{\lambda'}} \quad (4-65)$$

This expression is very similar to the first term in the free energy (3-13), the interband or internal-energy part. The second term (the entropy part) may also be obtained formally from the self-energy by consideration of the intraband $\lambda'=\lambda$ term. In (4-64) this term would just be zero for $E \neq 0$, but for $E=0$ we have to take into account that the phonon wave vector is nonzero. Denoting this part of the self-energy $\tilde{z}'_P(\vec{q}, E)$ and assuming for simplicity the matrix element to be independent of $\vec{q}$ for small $|\vec{q}|$, we find

$$\begin{aligned} \tilde{z}'_P(\vec{q}, E) &= 2 \sum_{\lambda \vec{k}} |H_{\lambda\lambda}^O(\vec{k})|^2 \frac{f(E_{\lambda}(\vec{k})) - f(E_{\lambda}(\vec{k}+\vec{q}))}{E+E_{\lambda}(\vec{k})-E_{\lambda}(\vec{k}+\vec{q})+is} \\ &\approx 2 \sum_{\lambda \vec{k}} |H_{\lambda\lambda}^O(\vec{k})|^2 \frac{df}{dE_{\lambda}} \frac{E_{\lambda}(\vec{k}) - E_{\lambda}(\vec{k}+\vec{q})}{E+E_{\lambda}(\vec{k})-E_{\lambda}(\vec{k}+\vec{q})+is} \end{aligned} \quad (4-66)$$

valid for $|E_{\lambda}(\vec{k}) - E_{\lambda}(\vec{k}+\vec{q})| \ll k_B T$. For small $\vec{q}$

$$E_{\lambda}(\vec{k}) - E_{\lambda}(\vec{k}+\vec{q}) \approx -\hbar \vec{v}_{\lambda} \cdot \vec{q} \quad (4-67)$$

where $\vec{v}_{\lambda}$ is the hole velocity, and so

$$\tilde{z}'_P(\vec{q}, E) \approx 2 \sum_{\lambda \vec{k}} |H_{\lambda\lambda}^O(\vec{k})|^2 \frac{df}{dE_{\lambda}} \frac{-\hbar \vec{v}_{\lambda} \cdot \vec{q}}{E - \hbar \vec{v}_{\lambda} \cdot \vec{q} + is} \quad (4-68)$$

For optic phonons $E \approx \hbar c_{\ell} |\vec{q}|$, where c_{ℓ} is the velocity of light, and since $c_{\ell} \gg v_{\lambda}$, the intraband contribution (4-68) is indeed very small for any value of E . This justifies the $\vec{q}=0$ approximation in (4-63) and (4-64).

For acoustic phonons, on the other hand, we have $E \approx \hbar c_s |\vec{q}|$, where c_s is the sound velocity, and since $c_s \ll v_{\lambda}$ for the majority of relevant holes, E is negligible in (4-68).

Setting formally $s=0$ we find for the total self-energy (including (4-65)):

$$\frac{1}{2} \text{Re} \tilde{z}'_P(0) = 2 \sum_{\lambda \vec{k}} \left\{ f(E_{\lambda}) \sum_{\lambda' \neq \lambda} \frac{|H_{\lambda\lambda'}^O(\vec{k})|^2}{E_{\lambda} - E_{\lambda'}} + \frac{1}{2} \frac{df}{dE_{\lambda}} |H_{\lambda\lambda}^O(\vec{k})|^2 \right\} \quad (4-69)$$

This is quite analogous to the free-energy expressions, e.g. (3-13) or (3-14), using the perturbation expressions (2-46) for the connection between energy changes δE_λ and matrix elements. We shall return to this point in a moment.

Of course, we cannot derive entropy changes in the free energy from considerations of the adiabatic self-energy. s is essentially the relaxation frequency of the hole and may be quite appreciable, so that $s=0$ is not valid. Assuming a mean-free-path l , we have $s = v/l$. Eq. (4-68) then shows that for acoustic phonons the self-energy approach is valid for $|\vec{q}|l \gg 1$, the region called nonlocal in Sec. 3.1. For the optic phonon case, similar arguments would demand $E \gg s$ or $\omega\tau \gg 1$ (τ being a hole relaxation time) as a condition for validity, but since (4-68) vanishes anyway, this is not necessary. Eq. (4-63) has no singularity for $E=0$.

Regarding the connection between the resonance energy shift $\text{Re}z_p(0)$ and the change in the elastic constant δC_{44} , we present the following similarity argument (originally devised by Cerdeira and Cardona (1972)). As shown in Chapter 2, a change in the (111)-bond $\delta \bar{r}_b$ can be produced either by an internal strain u_o or a (111) uniaxial strain $\epsilon_{yz} = \epsilon_{zx} = \epsilon_{xy} = \epsilon$. For the "optic" oscillator with eigenfrequency ω , the potential energy density is

$$\delta F_u = \frac{1}{2} \left(\frac{4}{3} \right) \left(\frac{1}{2} \rho \frac{a_c^3}{8} \right) \omega^2 |\delta \bar{r}_b|^2 = \frac{1}{8} \rho \omega^2 a_c^2 u_o^2 \quad (4-70)$$

since from (2-49) $|\delta \bar{r}_b| = u_o a_c$. For the (111)-strain we have (3-3)

$$\delta F_\epsilon = 6C_{44} \epsilon^2 \quad (4-71)$$

Now we have shown in (2-51) that for the same $\delta \bar{r}_b$

$$\frac{1}{2} u_o = \frac{\sqrt{3}}{4} \epsilon \quad (4-72)$$

Furthermore, for this situation the band splitting ΔE_{12} (2-52) is the same if (by definition) the deformation potentials satisfy

$$\frac{1}{4}d_o = d \quad (4-73)$$

The complete correspondence is then achieved for $\delta F_u = \delta F_e$, i.e.

$$\frac{1}{64} \rho \omega^2 a_c^2 = C_{44} \quad (4-74)$$

or

$$\delta C_{44} = \frac{1}{32} \rho \omega a_c^2 \delta \omega \quad (4-75)$$

$\delta \omega$ is obtained from $\text{Re} \tilde{z}_p$ in (4-69) by insertion of the matrix element (4-62):

$$\delta \omega = \frac{1}{\hbar} \text{Re} \tilde{z}_p(0) = \frac{2d_o^2}{\rho \omega a_c^2} \sum_{\lambda k} \left\{ \sum_{\lambda' \neq \lambda} \frac{f(E_{\lambda'})}{E_{\lambda} - E_{\lambda'}} g_{\lambda\lambda'}, + \frac{1}{2} \frac{df}{dE_{\lambda}} g_{\lambda\lambda} \right\} \quad (4-76)$$

Transformation of $\delta \omega$ to δC_{44} (4-75) and d_o to d (4-73) yields

$$\delta C_{44} = d^2 \sum_{\lambda k} \left\{ \sum_{\lambda' \neq \lambda} \frac{f(E_{\lambda'})}{E_{\lambda} - E_{\lambda'}} g_{\lambda\lambda'}, + \frac{1}{2} \frac{df}{dE_{\lambda}} g_{\lambda\lambda} \right\} \quad (4-77)$$

This expression is identical to (3-37) derived on a more direct basis.

Using an extrapolation (large $|\bar{q}|$) for the acoustic phonon dispersion we find an estimate of the optic frequency similar to (4-74)

$$\omega \approx \left(\frac{C_{44}}{\rho} \right)^{\frac{1}{2}} \frac{2\pi}{a_c} \quad (4-78)$$

Insertion in (4-76) and (4-77) then leads to the ratio (at $E=0$):

$$\left| \frac{\delta\omega}{\omega} \right| : \left| \frac{\delta C_{44}}{C_{44}} \right| \approx \left(\frac{d_o}{4d} \right)^2 \quad (4-79)$$

From transport data etc. we know the ratio on the right to be of the order of unity, and so the two relative changes on the left are of the same order of magnitude. Thus the enhancement for δC_{44} also occurs for $\delta\omega$.

4.4. Free holes in nonparabolic bands

We proceed to the actual calculation of the shift and broadening of the optic phonon based on eq. (4-63):

$$\hbar\delta\omega - i\Gamma = \text{Re}\tilde{z}_p(E) + i \text{Im}\tilde{z}_p(E) \quad (4-80)$$

evaluated for $E = \hbar\omega$, because there is no variation within an energy interval of the order of the relatively small shifts and broadenings encountered in this work.

By analogy with (3-50) for δC_{44} , we find using (4-62), (4-63), and (4-80)

$$\frac{\delta\omega}{\omega} = \frac{N_o d_o^2}{2\rho\omega^2 a_c^2 k_o T} \frac{1}{4\pi} \int d^2\hat{k} \frac{2}{\sqrt{\pi}} \int_0^\infty d\left(\frac{E}{k_o T}\right) \left(\frac{E}{k_o T}\right)^{\frac{1}{2}} \quad (4-81)$$

$$\times \sum_{\lambda=1}^3 \sum_{\lambda' \neq \lambda} f(E_\lambda) g_{\lambda\lambda'} k_o T \left\{ \frac{E_\lambda - E_{\lambda'} + \hbar\omega}{(E_\lambda - E_{\lambda'} + \hbar\omega)^2 + s^2} + \frac{E_\lambda - E_{\lambda'} - \hbar\omega}{(E_\lambda - E_{\lambda'} - \hbar\omega)^2 + s^2} \right\}$$

$$\frac{\Gamma}{\hbar\omega} = \frac{N_o d_o^2}{2\rho\omega^2 a_c^2 k_o T} \frac{1}{4\pi} \int d^2\hat{k} \frac{2}{\sqrt{\pi}} \int_0^\infty d\left(\frac{E}{k_o T}\right) \left(\frac{E}{k_o T}\right)^{\frac{1}{2}} \quad (4-82)$$

$$\times \sum_{\lambda=1}^3 \sum_{\lambda' \neq \lambda} f(E_\lambda) g_{\lambda\lambda'} \frac{4k_o T (E_\lambda - E_{\lambda'}) \hbar\omega s}{[(E_\lambda - E_{\lambda'} + \hbar\omega)^2 + s^2][(E_\lambda - E_{\lambda'} - \hbar\omega)^2 + s^2]}$$

We thus calculate the normalised quantities X_p (hole concentration) from (3-51) and (2-29), and Y and Z defined by (4-58).

For the front factor in (4-81) and (4-82)

$$f_o = \frac{N_o d_o^2}{2 \rho \omega a_c^2 k_o T} \cdot 10^3 = \xi \cdot \left(\frac{T}{300}\right)^{\frac{1}{2}} \left(\frac{d_o}{40 \text{ eV}}\right)^2 \quad (4-83)$$

where the material parameters for Ge and Si are listed in Table 4.6. The small, positive, constant s is chosen so that the numerical results are independent of the actual choice. In order to achieve an error smaller than 0.1%, the total number of (E^*, k) sets needed was equivalent to 360000 $\bar{k}$ points.

Table 4.6. Relevant material parameters for Ge and Si.

Material:	Si	Ge
$\rho (10^3 \text{ kgm}^{-3})$	2.33	5.33
$\hbar\omega$ (meV)	65	37
a_c (Å)	5.43	5.66
ξ	18.3	22.8

The results for silicon at $T = 77$ and 300K are shown in Tables 4.7 and 4.8, respectively. They are compared with the experimental data (which were given in Tables 4.1 through 4.4) in Figs. 4.9 and 4.10. The overall fit, in particular at the higher concentrations $X > 6$, yields the value of the optic deformation potential $d_o = 27 \text{ eV}$. Although some details are not entirely satisfactory, one should bear in mind that both the real and the imaginary parts of the self-energy are fitted by using the single parameter d_o over almost two decades of hole concentrations.

There are two points to be made about the data for $X < 6$, where the experimental data depart from theory. For this region the calculated chemical potential lies in the interval from -40 to $+40 \text{ meV}$ relative to the band edge, and this

Table 4.7. Nonparabolic calculation of Y and Z for Si at 77K. $d_o = 27$ eV corresponding to the best fit to experimental data.

μ (meV)	X_p	Y	Z
-10.0	0.043	-0.091	0.096
-5.0	0.083	-0.173	0.187
0.0	0.16	-0.31	0.36
3.0	0.23	-0.42	0.53
6.0	0.32	-0.55	0.74
11.0	0.53	-0.78	1.22
15.5	0.79	-0.98	1.81
21.5	1.25	-1.19	2.80
30.0	2.15	-1.21	4.6
40.0	3.6	-0.61	7.1
50.0	5.3	0.84	9.7
60.0	7.4	3.4	12.3
70.0	9.8	6.9	14.1
90.0	15.2	14.9	14.1
125.0	26.7	22.1	7.8
200.0	58.	26.5	4.6
300.0	110.	30.	1.06

Table 4.8. Nonparabolic calculation of Y and Z for Si at 300K. $d_o = 27$ eV corresponding to the best fit to experimental data.

μ (meV)	X_p	Y	Z
-50.	0.35	0.096	0.50
-25.	0.88	0.278	1.22
0.	2.07	0.83	2.68
20.	3.8	1.92	4.5
35.	5.7	3.4	6.0
50.	8.1	5.4	7.6
75.	13.5	9.9	9.2
125.	28.4	18.6	8.1
200.	59.	25.5	4.4
300.	111.	30.	1.59

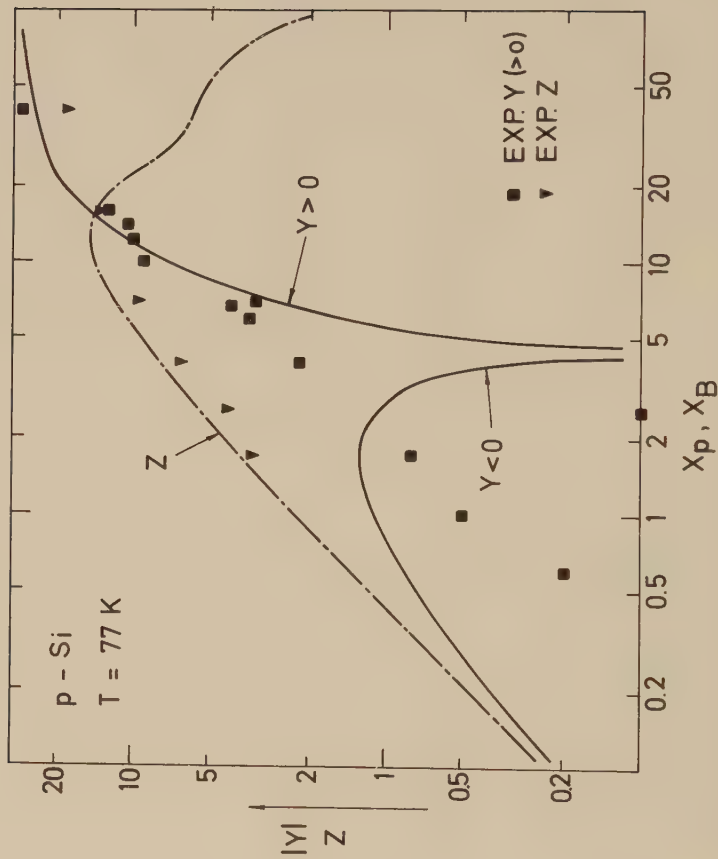


Figure 4.9. Theoretical and experimental results for Y and Z in Si at 77K as function of hole (or impurity) concentration X . The fit of Y at the higher concentrations (in combination with Fig. 4.10) yields $d_0 = 27\text{ eV}$.

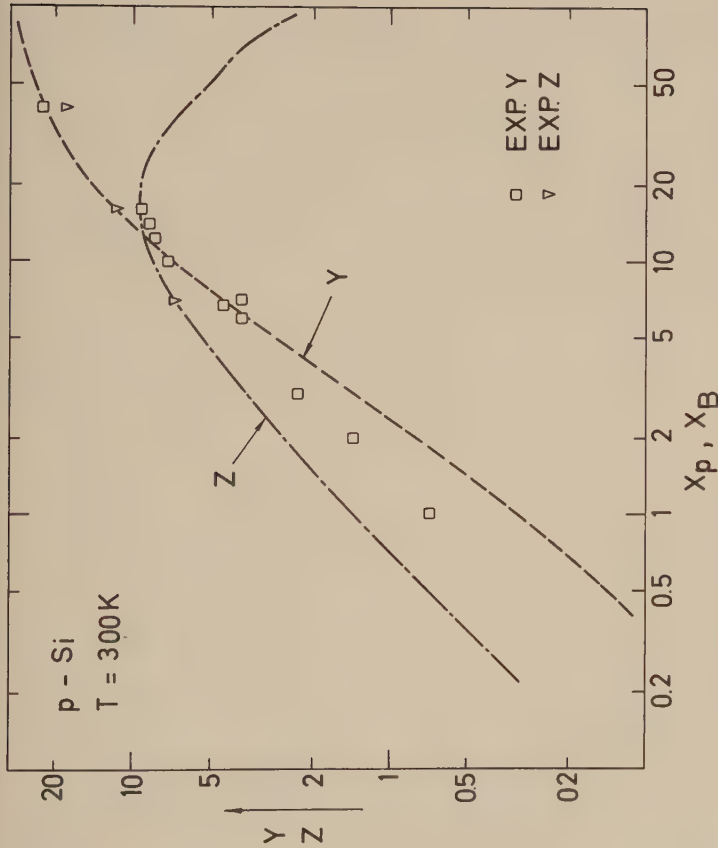


Figure 4.10. Theoretical and experimental results for Y and Z in Si at 300K as function of hole (or impurity) concentration X. The fit of Y at the higher concentrations (in combination with Fig. 4.9) yields $d_0 = 27$ ev.

is exactly where we expect considerable band distortions due to the impurities, cf. Sec. 2.3.

The first point is that the semilocalised nature of the mixed band-impurity states may result in peculiar hole-transport properties with no simple connection between hole concentration on the one side and conductivity and Hall effect on the other. Thus the experimental determination of the carrier concentration (which is described extremely little in the various pertinent references) may not be reliable, and we expect that such an effect would result in an underestimate. Indeed, Fig. 4.10 indicates a systematic error in the hole concentrations for $X = 1.0, 2.0$, and 3.0 where a 50% raise would bring the data into consistency at 300K. Applying a similar correction to the data in Fig. 4.9 (77K), we obtain a much improved fit to the steep rise around $X = 5-6$.

The second point concerns the behavior of Y around $X = 1-2$ at 77K. At first sight, the agreement between theory and experiment is not bad, i.e. both have local maximum at the same concentration. However, the two have opposite signs in this region, and so the discrepancy $Y_{\text{exp}} - Y_{\text{theor}}$ has a pronounced maximum near $X = 2$. What could cause this extra shift? One possible explanation is that the distortion makes some of the intervalence-band gaps (hole transition energies) greater than for the ideal crystal by lowering the heavy-hole band states. This makes the shift go in the right direction, but our ignorance of the real situation prevents quantitative detail in this argument.

At very high carrier concentrations a possible departure from $Y \propto X^{1/3}$ could be ascribed to direct second-order terms $Y \propto X$. The absence of this feature in Figs. 4.9 and 4.10 puts an upper limit to the second-order optic deformation potential. An estimate shows that the second-order potential is not higher than what would be called normal, i.e. for a hypothetical internal strain yielding $|\delta \bar{r}_b| / |\bar{r}_b| \sim 1$, the first and the second order change in the electronic potential would be of equal magnitude. Of course, in this high-concentration region it is perhaps amazing that other secondary effects do

not show up. At $p = 4 \cdot 10^{20} \text{ cm}^{-3}$ the so-called enhancement is apparently still of the order of 10.

The experimental data on the broadening do not show any tendency to drop off at high concentration. This theoretical feature is due to final-state occupation which kills the absorption of the optic phonon. This feature, $\Gamma_{\text{exp}} \gg \Gamma_{\text{theor}}$, will be very prominent for Ge and may be another effect of the impurity-induced distortion.

Table 4.9 Nonparabolic calculation of Y and Z for Ge at 77K. $d_0 = 27 \text{ eV}$ according to fit in Fig. 4.11.

$\mu \text{ (meV)}$	X_p	Y	Z
0.	0.06	0.14	0.13
20.	0.33	0.99	0.40
40.	0.88	2.21	0.30
75.	2.41	4.2	0.04
125.	5.9	7.8	0.05
200.	14.8	13.4	0.07
300.	33.	18.7	0.10

The results for germanium at $T = 77$ and 300K are shown in Tables 4.9 and 4.10, respectively. This is calculated for the complete nonparabolic band model. For comparison, we list in Table 4.11 some results for a corresponding parabolic two-band model which was originally thought to be adequate for Ge at lower hole concentrations. They are all shown in Fig. 4.11 along with the experimental data from Table 4.5. We have not plotted the values of Z since it is evident from the tables that the experimental values are an order of magnitude larger than the theoretical ones. We shall return to this point in a moment.

Table 4.10. Nonparabolic calculation of Y and Z for Ge at 300K. $d_{O_2} = 27$ eV according to fit in Fig. 4.11.

μ (meV)	X_p	Y	Z
0.	0.49	0.98	0.14
20.	0.88	1.63	0.16
40.	1.47	2.54	0.20
75.	3.1	4.5	0.12
125.	6.7	7.9	0.09
200.	15.6	13.2	0.11
300.	34.	18.4	0.13

Table 4.11. Parabolic two-band model results for Y and Z in Ge at 300K. $d_O = 27$ eV for the purpose of comparison

μ (meV)	X_p	Y	Z
0.0	0.40	0.35	0.10
12.1	0.58	0.45	0.12
33.3	1.00	0.68	0.12
67.1	2.00	1.06	0.08

We observe in Fig. 4.11 that a parabolic two-band model is a bad approximation in Ge for the present problem, though one would apriori expect it to be quite reasonable because of the large spin-orbit splitting. The same feature was evident in δC_{44} .

The concentration dependence of the calculated values of Z is at first sight rather strange, i.e. first a maximum at $X \sim 0.5-1$, then a minimum followed by a rise at higher concentration. The relatively small value of $Z \ll Y$ and the maximum are connected with the killing of the phonon absorption by

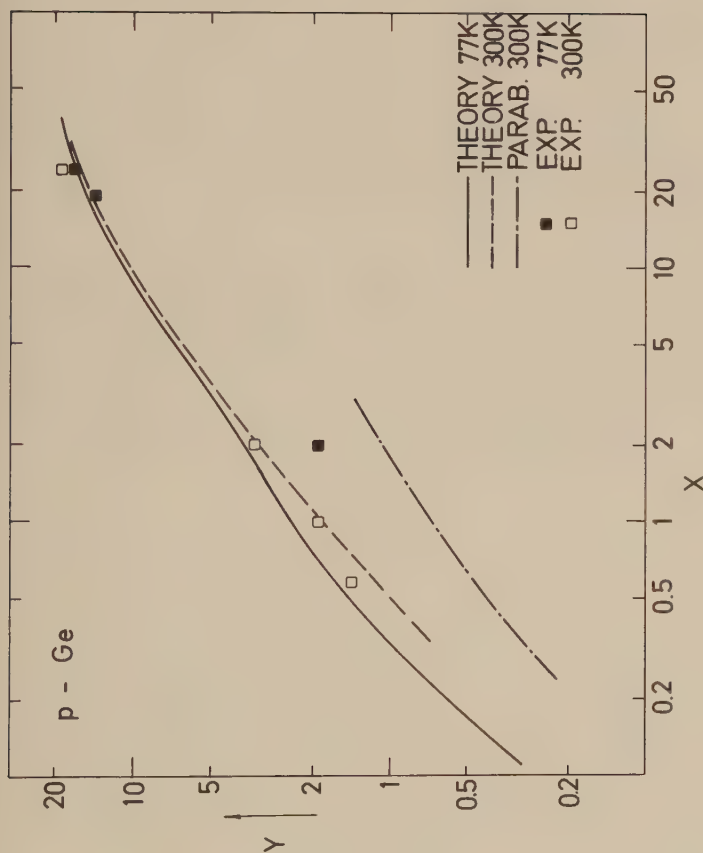


Figure 4.11. Theoretical and experimental values for Y in Ge at 77 and 300K as function of hole (or impurity) concentration X. The fit at the highest concentrations yields $d_0 = 27$ eV.

final-state occupation which sets in at low concentrations because of the small value of $\hbar\omega$. The rise at higher concentrations is an artifact of the calculation and is related to the special choice of the secondary broadening s , which in our calculations was taken to be

$$s = \frac{5}{600} (\mu + 6k_B T) / (A + \frac{B}{2} - \frac{3}{2} \frac{D}{\sqrt{3}}) \quad (4-84)$$

for $\mu > 0$. Z will then be proportional to s and in this way dependent on concentration in the indirect absorption region. This is the observed feature, and its small magnitude illustrates that such computational artifacts are generally unimportant.

Our theory for Y fits the data at high concentrations (where they would be most reliable according to the discussion in Sec. 4.3) for $d_0 = 27$ eV. The general agreement is quite good for $T = 300$ K, but less so at $T = 77$ K. Again band-edge distortions can be forwarded as a likely explanation, but without further qualification. As long as the discrepancy for Z remains unexplained, the reliability of $d_0 = 27$ eV can be questioned.

A good deal of work has gone into repairing the deficiency around Z (or Γ). Our analysis of the Fano effect in Sec. 4.3 showed that Γ_{theor} is probably representative of the coupling of the optic phonon to vertical hole excitations, and so $\Gamma_{\text{obs}} - \Gamma_{\text{theor}}$ must be ascribed to decay processes not contributing to the Fano effect. Thus ordinary indirect absorption is excluded (and is indeed very small for realistic values of s due to impurity and phonon scattering). Another possibility is the interference between two second-order decay processes having different intermediate (resonant) hole-excitation states (vertical transitions at different $\bar{k}$ ending up in the same final state after the secondary scattering). Such an effect was treated by Lawaetz et al. (1972) for a different situation (cf. Sec. 5.2), and it was shown that nothing spectacular will result. Actually, Γ_{theor}

calculated by the golden-rule formula and disregarding final-state occupation will still be much smaller than Γ_{obs} . The main reason is that the phonon-hole resonance occurs rather close to $\bar{k} = 0$ where the combined density-of-states is small. This is a result of the conservation of wave vector demanding vertical hole transitions.

An additional broadening caused by possible inhomogeneous doping would smear out any trace of the Fano effect and is therefore not pertinent.

The possibility of $\bar{q}$ being no good quantum number in Ga-doped Ge was dismissed in Sec. 2.3 since the mass fluctuation would be smaller than that due to the isotopic mixture in pure Ge.

We are left with the acceptor-induced $\bar{k}$ -vector mixing discussed in Sec. 2.3. This mechanism will break up the strict momentum-conservation condition and thus allow for nonvertical hole transitions. A simulation of this effect is performed in the next section. Although this could increase Γ_{total} in accord with observation, it is not clear why the hole-excitation Raman continuum is not similarly increased so that the Fano spectrum parameter q fulfils $q\Gamma_{\text{total}} = \text{cst.}$, which is not observed, cf. Sec. 4.3. This may be a question of whether the complex $\tilde{q}$ has an imaginary component.

4.5. Simulation of impurity-distorted bands

The above theory of the shift and broadening for Ge is unsatisfactory in two ways: It provides no explanation for the observed behavior of Γ , and the fit for $\delta(\hbar\omega)$ gives a value of d_0 which is too small to account for the phenomena discussed in Sec. 5.2.

One of the possible effects of impurity - induced distortion is that the wave vector $\bar{k}$ of the hole is no longer well defined within a certain region of $\bar{k}$ -space around $k=0$. This idea is not easily introduced into our theory, but we can approximately simulate the effect by smearing the phonon wave vector $\bar{q}$ instead. Thus we calculate the $\bar{q}$ -dependent

self-energy of the phonon for an ideal crystal and subsequently take an average over a suitable part of $\bar{q}$ -space.

The generalisation of eq. (4-64) to nonvanishing $\bar{q}$ is straightforward:

$$\bar{z}_p(\bar{q}, E) = 2 \sum_{\lambda \lambda' \bar{k}} |H^0(\lambda \bar{k}, \lambda' \bar{k} + \bar{q})|^2 \frac{f(E_\lambda(\bar{k})) - f(E_{\lambda'}(\bar{k} + \bar{q}))}{E + E_\lambda(\bar{k}) - E_{\lambda'}(\bar{k} + \bar{q}) + i\epsilon} \quad (4-85)$$

Note that the intraband contribution has now been included. The squared matrix element in (4-85) can be worked out by the methods described in the appendices, but considering the approximate character of the model, it is not worth while to go to such detail. Consequently, we set $\bar{q}=0$ in the matrix element in the expectation that the major $\bar{q}$ dependence results from the last energy factor. By this approximation we also neglect the dependence of $\bar{z}_p$ on phonon polarisation, but since we shall average in the end anyway, this is of little importance. The shift due to ordinary dispersion is also ignored because it is intrinsic. So for the present purpose,

$$\bar{z}_p(\bar{q}, E) \approx 2 \sum_{\lambda \lambda' \bar{k}} |H^0_{\lambda \lambda'}(\bar{k})|^2 \frac{f(E_\lambda(\bar{k})) - f(E_{\lambda'}(\bar{k} + \bar{q}))}{E + E_\lambda(\bar{k}) - E_{\lambda'}(\bar{k} + \bar{q}) + i\epsilon} \quad (4-86)$$

where $|H|^2$ is the same as used previously in (4-64). The computational formulas then follow by analogy with (4-81) and (4-82):

$$\begin{aligned} \frac{\text{Re} \bar{z}_p(\bar{q}, \hbar\omega)}{\hbar\omega} &= \frac{N_0 d_0^2}{2\rho\omega^2 a_c^2 k_0 T} \frac{1}{4\pi} \int d^2\hat{k} \frac{2}{\sqrt{\pi}} \int_0^\infty d\left(\frac{E^*}{k_0 T}\right) \left(\frac{E^*}{k_0 T}\right)^{\frac{1}{2}} \\ &\times \sum_{\lambda, \lambda'=1}^3 g_{\lambda \lambda'}(\bar{k}) \left[f(E_\lambda(\bar{k})) - f(E_{\lambda'}(\bar{k} + \bar{q})) \right] \frac{k_0 T (E_\lambda - E_{\lambda'} + \hbar\omega)}{(E_\lambda - E_{\lambda'} + \hbar\omega)^2 + s^2} \end{aligned} \quad (4-87)$$

$$\frac{-\text{Im}\tilde{Z}_P(\bar{q}, \hbar\omega)}{\hbar\omega} = \frac{N_O d_O^2}{2\rho\omega^2 a_C^2 k_O T} \frac{1}{4\pi} \int d^2\hat{k} \frac{2}{\sqrt{\pi}} \int_0^\infty d\left(\frac{E}{k_O T}\right) \left(\frac{E}{k_O T}\right)^{\frac{1}{2}} \\ \times \sum_{\lambda, \lambda'=1}^3 g_{\lambda\lambda'}(\bar{k}) \left[f(E_\lambda(\bar{k})) - f(E_\lambda(\bar{k}+\bar{q})) \right] \frac{k_O T s}{(E_\lambda - E_\lambda + \hbar\omega)^2 + s^2} \quad (4-88)$$

We calculate (4-87) and (4-88) in parts per thousand, i.e. the quantities Y and Z defined in (4-58). The wave vector $\bar{q}$ is taken parallel to the cubic axes (100) and its magnitude is given by the equivalent energy

$$E_q = \frac{\hbar^2}{2m} |\bar{q}|^2 \quad (4-89)$$

For the absorptive part $Z(\bar{q})$, there will be significant variations only in the interval $0 < |\bar{q}| < 2k_F$, where $2k_F$ is the maximum distance across the heavy-hole Fermi surface. However, singularities in the combined density of states are most prominent at smaller $|\bar{q}|$ as indicated in Fig. 4.12. Furthermore, we believe that the region of interest in the present impurity-distortion model is $|\bar{q}| \lesssim 2/a_B$ where a_B is the Bohr radius of the acceptor ground state in a simple hydrogenic model with the same binding energy. For Ge we thus find $E_{q, \max} \approx 10$ meV.

The results for Ge at $T=77K$, three different hole concentrations, and $\bar{q} \parallel (100)$ are shown in Fig. 4.13, which presents the main variation in a region of E_q scaling with the chemical potential μ , and in Fig. 4.14, which exhibits the behavior for $E_q < 10$ meV on a linear wave vector scale. The curves are drawn according to a "principle of minimum amplitude and complexity" and following the analytical property of alternating extrema in Y and Z. (In Fig. 4.14, extrema in one curve coincide with points of inflection in the other).

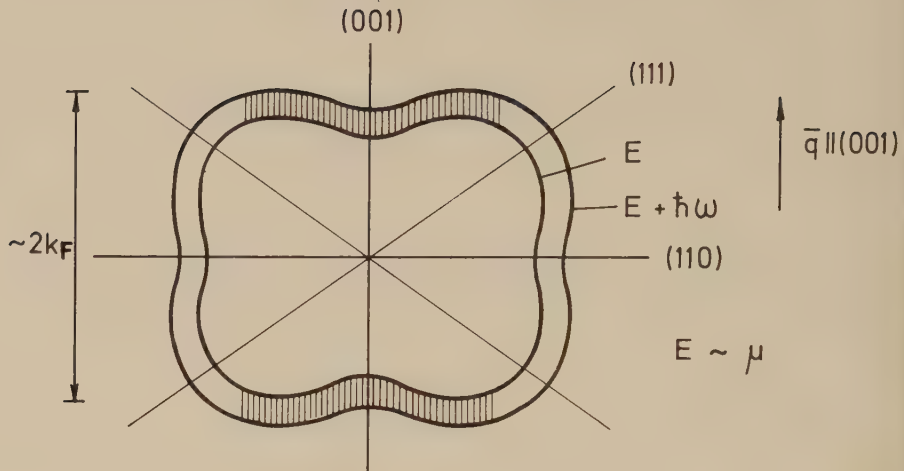


Figure 4.12. $(1\bar{1}0)$ -plane cross-section of surfaces of constant heavy-hole energy (in Ge) showing the maximum $|\bar{q}| \sim 2k_F$ for absorption of a phonon $(\bar{q}, \hbar\omega)$ and typical singularities in the combined density of states (shaded areas).

The result is an amazing richness of structure due to the anisotropy of the hole bands. It is a pity that this is outside the domain of experimental detection at present. Here, we average $Y(q)$ and $Z(q)$ over the first 10 meV in E_q , and since we are ignorant as to the "spectral" distribution of E_q , we assign equal weights to all points on the linear q -scale in Fig. 4.14. For $\bar{q} \parallel (100)$, we find the averages $\langle Y \rangle$ and $\langle Z \rangle$ listed in Table 4.12, calculated for $d_0 = 27$ eV.

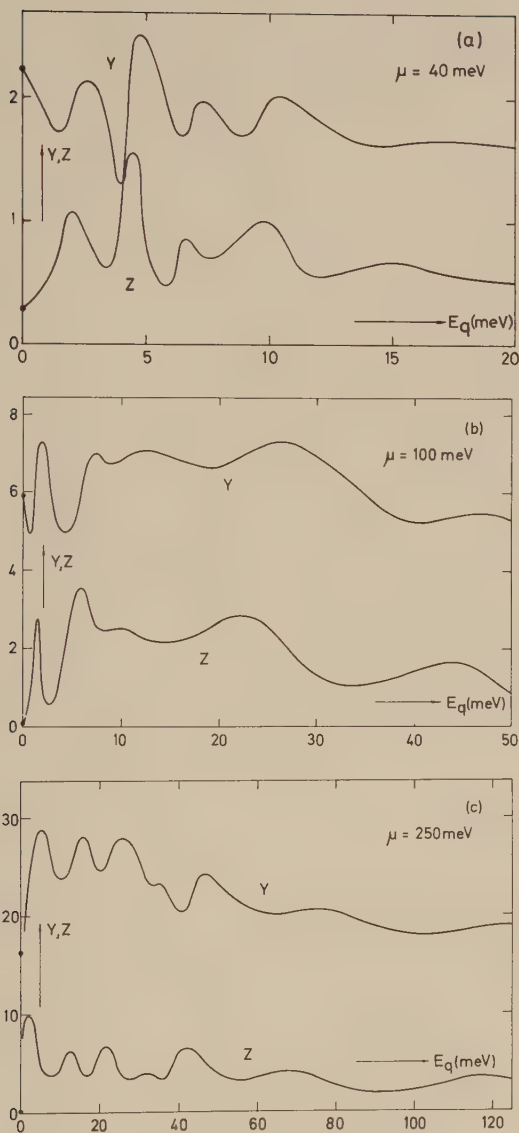


Figure 4.13. $\bar{q}$ -dependence of the shift Y and broadening Z of the optic phonon in Ge at 77K. $\bar{q} \parallel (100)$ and quadratic (energy) scale. The hole concentrations are (a) 0.88, (b) 3.94, and (c) 23.0, all in units of 10^{19} cm^{-3} . $d_0 = 27$ eV.

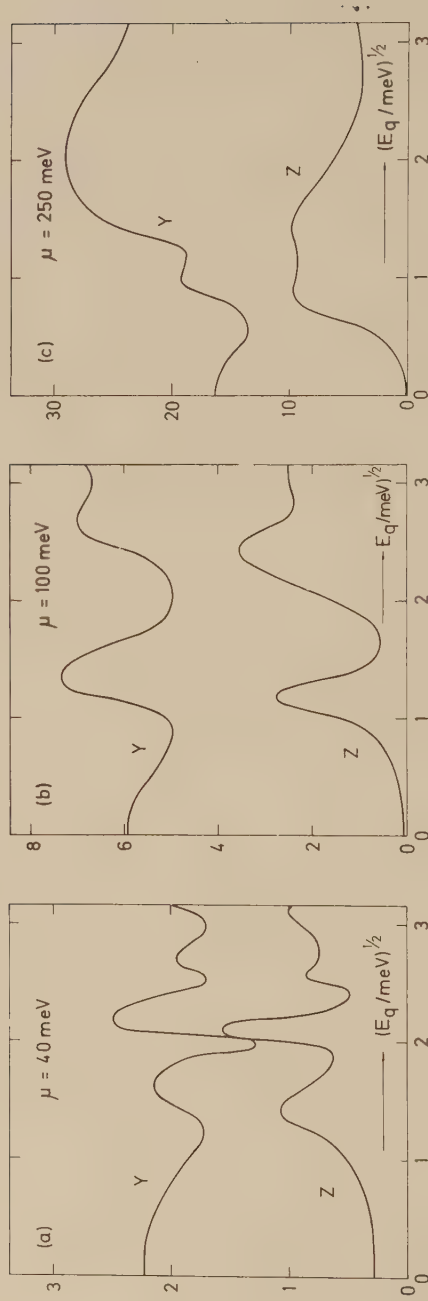


Figure 4.14. $\bar{q}$ -dependence of shift and broadening of the optic phonon in Ge at 77K. $\bar{q} \parallel (100)$ and linear (wave vector) scale. The hole concentrations are as in Fig. 4.13. $d_0 = 27 \text{ eV}$.

Table 4.12. Average shifts $\langle Y \rangle$ and broadenings $\langle Z \rangle$ for $E_q \leq 10$ meV in Ge at 77K. $d_o = 27$ eV.

μ (meV)	X	$\langle Y \rangle$	$\langle Z \rangle$
40	0.88	1.97	0.66
100	3.9	5.9	1.47
250	23.0	22.2	5.6

These averages should have been taken over all directions of $\bar{q}$. However, for a number of reasons, this was not considered worth while. First of all, the character of the distortion model is such that the results are only semi-quantitative. Secondly, we do not expect a drastic anisotropy in $[\langle Z \rangle]_{\bar{q}}^{\hat{q}}$ because for fixed μ , $k_o T$, and $\hbar\omega$, each $\bar{k}$ -point gives the same contribution to the integrated absorption $[\int_0^\infty Z(\bar{q}) dE_q]_{\bar{q}}^{\hat{q}}$, which is thus independent of $\hat{q}$. The present average $\langle Z \rangle$ is over a limited range of E_q , but this will not lead to much anisotropy. A similar feature holds for $\langle Y \rangle$ because the variations in Y and Z are coupled. Finally, the fluctuations in $Y(q)$ and $Z(q)$ must lead to a non-Lorentzian shape of the resulting Raman spectra, and so the parameters $\langle Y \rangle$ and $\langle Z \rangle$ are not uniquely related to to experiment anyway. A complete analysis including the Fano-type complications (the free-hole Raman intensity varies similar to $Z(\bar{q})$) should await a theory of the $\bar{q}$ -distribution and also more detailed experimental information.

The results in Table 4.12 are compared in Fig. 4.15 with experimental data from Table 4.5. It is obvious that the order-of-magnitude agreement has been improved considerably for Z, and that $d_o = 27$ eV is still a reasonable fit for Y. The disparity between $d_o = 27$ eV obtained here and the value $d_o = 39$ eV found in Chapter 5 remains to be analysed at a later stage. We find that the two should actually be different as a consequence of spin-orbit effects.

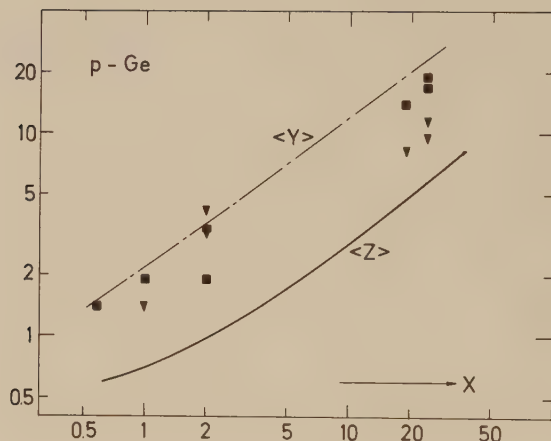


Figure 4.15. $\langle Y \rangle$ and $\langle Z \rangle$ for Ge at 77K compared with available experimental data. X is the normalized hole concentration. Experimental data at 300K are included because there should be little difference above $X=1$. Squares: Y_{exp} , triangles: Z_{exp} (extrinsic value).

A final point to be made here is that we ought to consider similar impurity-induced effects in Si. However, except for the highest attainable hole concentrations, the relatively high value of $\hbar\omega$ (65 meV) combined with the small band parameters leads to very little variation of Y and Z with E_q . Only in the very large concentration range, where the calculated $Z(\bar{q}=0)$ drops off by contrast to the experimental data, the distortion effects may play a significant role and make theory follow experiment more closely.

The present model of the influence of impurity-induced distortion set out on the assumption of k -vector smearing, but for practical reasons this was replaced by a spread in the q -vector. Perhaps there is more truth in this consideration so that the spread is a real manifestation of strong impurity scattering. The application of the model to Ge has provided more realistic theoretical values of the hole-induced phonon broadening, but it has also shown that the resonance shifts are reasonably well produced by considering $\bar{q}=0$ only. The latter feature is expected to hold as long as $\hbar\omega$ is much larger than the hole-broadening parameter s (cf. eq. (4-85)), which has so far been chosen conveniently small. Actually, our calculations couple s to μ , and so for case (c) above ($\mu = 250$ meV), $s \approx 5$ meV is no longer so small compared with $\hbar\omega = 37$ meV, and $\langle Y \rangle$ departs from $Y(q=0)$.

We have everywhere considered $\bar{q}=0$ a good approximation in the Raman-scattering experiments on ideal crystals. Actually $|\bar{q}|$ is not that small. For the laser wavelength $\lambda_L = 4880$ Å used in the experiments on Ge in the backscattering configuration (Cerdeira and Cardona 1972), the photon wave vector in the material is $|\bar{k}| \approx 5 \cdot 10^5 \text{ cm}^{-1}$, which leads to $|\bar{q}| = 2|\bar{k}| = 10^6 \text{ cm}^{-1}$ and $E_q \approx 0.3$ meV. We conclude from inspection of Fig. 4.14 that E_q is just small enough for $\bar{q}=0$ to be a good approximation. The observed effects could not arise in this way.

5. OTHER PARTS OF THE PHONON SPECTRUM

So far we have studied the influence of certain electronic excitations (presence of free holes in thermal equilibrium near the valence-band edge) on long-wavelength vibrational or phonon resonances. The carrier excitations were produced by doping. The investigation can be generalised in two principal ways (staying within the subject of carriers near the valence-band edge): other forms of excitations in the electronic system, and other parts of the phonon spectrum. We shall do both in order to match up with relevant physical situations.

The excitation of holes in or into the valence band will produce changes in the phonon resonances not only at long wavelengths, but rather over the whole Brillouin zone. Provided that these phonon states are to some extent occupied, a single hole excitation will produce a change in energy of the phonon gas, and this energy is added to the original excitation energy, e.g. the band gap, so that the total excitation energy is that of the crystal as a whole. Since the phonon state occupation is dependent on temperature, we thus get a temperature dependence of the band gap and other electronic excitation energies. In other words: Just as electronic excitations influence the phonon spectrum, the phonon excitations influence the electronic spectrum.

This way of tracing the temperature dependence to phonon changes effected by the carrier excitation was proposed by Heine and Van Vechten (1976) and is worked out in more detail in Sec. 5.1. Our main purpose is to elucidate the difference between the optical energy gaps and thermal gaps and to resolve the old problem of the temperature dependence of the band structure near the band edge, i.e. of the effective-mass parameters.

Since we do not know the parameters of the electron-phonon interaction at general wave vectors $\vec{q}$, it is not possible

to calculate the above temperature dependence quantitatively. However, certain related phenomena only involve a limited region of $\bar{q}$ space, in particular the long-wavelength region, and such a case is studied in Sec. 5.2. This concerns the different resonance behavior of two optical excitations, the E_0 and $E_0 + \Delta_0$ structure in the interband spectrum. The difference in shift can be related to an electron-phonon contribution to the spin-orbit splitting, and the difference in broadening to lifetime broadening of the split-off hole due to interaction with optic phonons. From experimental data it is then possible to extract information on the multipole contribution to the electron-phonon interaction, and by this means the full picture of the coupling between holes and optic phonons is obtained.

5.1. Temperature dependence of band structure

The minimum energy gaps between conduction and valence bands shows up experimentally in the intrinsic carrier concentration and in the optical properties. It has been known for a long time that the gap depends on temperature. One contribution to this variation comes from thermal expansion and is readily calculated from known parameters. (It has been separated out in the following). However, the dominant (so-called explicit) contribution is due to the electron-phonon interaction, and since the early calculation by Fan (1951), many papers have been devoted to this subject.

Until recently, there has been much confusion because the Fan theory (second-order perturbation) could not be evaluated quantitatively and appeared to give shifts of one sign only, the alternative Brooks-Yu theory (thermal damping of pseudopotential form factors, no original reference, see Keffer et al. (1968)) was not always in agreement with experiment, and some people even suggested that the results of the two theories should be added (Baumann 1972, Schlüter et al. 1975). The main reason for this uncertainty is essentially that the basic adiabatic approximation (division between electronic

and vibrational systems) was not clearly defined. Our choice of adiabatic approximation is outlined in Appendix B.

The thermal band gap is the difference in free energy between the crystal in the state with an electron-hole pair at the band edges and in the ground state. The explicit temperature dependence arises from the thermal population of the phonon spectrum combined with the change in this spectrum effected by the electronic excitation. This point of view was suggested by Heine and Van Vechten (1976) by reference to remarks by Brooks (1955). For the temperature dependence we then find

$$\begin{aligned} E_g(T) - E_g(0) &= \delta \left\{ k_0 T \sum_i \ln \left[1 - \exp\left(-\frac{\hbar\omega_i}{k_0 T}\right) \right] \right\} \\ &= k_0 T \sum_i \ln \left(\frac{1 - \exp\left(-\frac{\hbar\omega_i'}{k_0 T}\right)}{1 - \exp\left(-\frac{\hbar\omega_i}{k_0 T}\right)} \right) \end{aligned} \quad (5-1)$$

where i denotes the phonon mode and

$$\omega_i' = \omega_i + \delta\omega_i \quad (5-2)$$

is the changed frequency of the mode due to the electron-hole pair excitation. Since $|\delta\omega_i| \ll \omega_i$, we expand (5-1) and obtain for the thermal gap

$$E_g(T) - E_g(0) = -k_0 T \sum_i \frac{\hbar\omega_i}{k_0 T} n(\omega_i) \left(-\frac{\delta\omega_i}{\omega_i}\right) \quad (5-3)$$

$$= \sum_i n(\omega_i) \delta(\hbar\omega_i) \quad (5-4)$$

where $(i \sim \vec{q}, s)$

$$n(\omega_i) = \left[\exp\left(\frac{\hbar\omega_i}{k_0 T}\right) - 1 \right]^{-1} \quad (5-5)$$

is the thermal equilibrium number of phonons in the mode i . The formulas (5-3) and (5-4) are exact, but the problem is not yet solved. Heine and Van Vechten (1976) calculated $(-\delta\omega_i/\omega_i)$ using a crude bond-charge model which we shall not pursue. One of their interesting results is that the change $|\delta\omega_i|$ produced by one electron-hole pair (in particular the hole) is relatively large because of the strong bonding character of states near the valence-band edge. (The correspondingly strong dependence $E_g(T)$ is confirmed by experiment). Thus the enhancement discussed previously in this work appears again, but now for a general phonon wave vector. The basic reason is the strong hole-phonon coupling combined with the small band width of the valence bands close to the edge. This can be seen from the Fan-type expression (second-order perturbation)

$$\begin{aligned} \delta(\hbar\omega_{\vec{q}s}) = \sum_{\lambda} |H_S(0 \rightarrow \lambda\vec{q})|^2 & \left\{ (E_O - E_{\lambda\vec{q}} + \hbar\omega_{\vec{q}s})^{-1} \right. \\ & \left. + (E_O - E_{\lambda\vec{q}} - \hbar\omega_{\vec{q}s})^{-1} \right\} \end{aligned} \quad (5-6)$$

which in our formulation must be dominant since we know from the previous chapters that the direct second-order contribution (connected with W_{nn} in (B-5)) has a "normal" magnitude. Thus Fan was right, but his successors forgot to let λ cover more than one band, which can be quite important especially for small-gap materials, where interband terms can make the sign change.

It is interesting to add the temperature-independent spontaneous emission term to (5-4) and (5-6) in order to obtain the total phonon contribution to the band gap

$$\begin{aligned} \delta E_g^{\text{ph}} = \sum_{\lambda\vec{q}s} |H_S(0 \rightarrow \lambda\vec{q})|^2 \\ \times \left\{ \frac{n_{\vec{q}s}}{E_O - E_{\lambda\vec{q}} + \hbar\omega_{\vec{q}s}} + \frac{n_{\vec{q}s} + 1}{E_O - E_{\lambda\vec{q}} - \hbar\omega_{\vec{q}s}} \right\} \end{aligned} \quad (5-7)$$

For the majority of modes contributing to (5-7), the $\hbar\omega$ in the denominators is negligible

$$\delta E_g^{ph} \approx \sum_{\lambda \bar{q}s} |H_s(0 \rightarrow \lambda \bar{q})|^2 \frac{2n_{\bar{q}s}^- + 1}{E_o - E_{\lambda \bar{q}}} \quad (5-8)$$

In the high-temperature region where $\hbar\omega_{\bar{q}s}^- \ll k_o T$ we have

$$n_{\bar{q}s}^- \approx \frac{k_o T}{\hbar\omega_{\bar{q}s}^-} - \frac{1}{2} \quad (5-9)$$

so that δE_g^{ph} is linear in temperature. Extrapolation to $T = 0$ yields a way of determining the bare electronic band gap E_{go} which is in fact identical to the linearly extrapolated gap. The extrapolation is, however, somewhat inaccurate because the condition $\hbar\omega_{\bar{q}s}^- \ll k_o T$ is not easily achieved. For Si the data compiled by Heine and Van Vechten (1976) indicate $\delta E_g^{ph}(0) \approx -160$ meV, and this value is probably representative of most ordinary semiconductors.

A crude theoretical estimate of $\delta E_g^{ph}(0)$ can be obtained by the following approximate model of contributions: hole only, three optic phonon branches, hole-phonon interaction described by a constant matrix element having the value at $\bar{q} = 0$, and $E_{\lambda \bar{q}} - E_o$ replaced by an average hole-energy jump Δ . In this model, application of (5-8) and (B-19) give for unit volume

$$\delta E_g^{ph}(0) \approx - \sum_{\bar{q}} \frac{3\hbar d_o^2}{2\rho\omega a_c^2 \Delta} \quad (5-10)$$

The number of $\bar{q}$ states in unit volume is equal to the number of unit cells $4/a_c^3$:

$$\delta E_g^{ph}(0) \approx - \frac{6\hbar d_o^2}{\rho\omega a_c^5 \Delta} \quad (5-11)$$

which for typical Si-parameters, $d_o = 27$ eV and $\Delta \approx 1.0$ eV, yields $\delta E_g^{ph}(0) \approx -60$ meV in qualitative agreement with the experimental result. It is noteworthy that the relative

contribution from the $q = 0$ optic phonon is about 8 times greater since the energy jump is $\Delta_0 + \hbar\omega \approx 120$ meV.

Electronic band-structure calculations for semiconductors have reached an accuracy better than 100 meV (according to more modest claims) by introduction of nonlocal pseudopotentials (Chelikowsky and Cohen 1976). The potential parameters are chosen so that characteristic optical structures at low temperatures are matched by theory. We wish to make the point here that since the phonon renormalisation of electronic energies, e.g. $\delta E_g^{\text{ph}}(0)$, is not explicitly included in the theory, but enters the experimental data, the fitted pseudopotentials cannot be physically accurate. Considering the magnitude of $\delta E_g^{\text{ph}}(0)$, we conclude that the present accuracy is not likely to be improved without taking the appreciable phonon contribution explicitly into account.

The above discussion was based on the free-energy gap, whereas most of the experimental data at room temperature and below are relevant for the optical band gap, i.e. a specific structure seen in the optical spectrum. Brooks (1955) showed the equality of the free-energy and the optical gap, but his proof was based on an incorrect form of the electron-phonon coupling, and nobody has bothered about this important problem since. We show in the following that the two gaps are identical.

The electron-phonon coupling contributes to the optical gap in two ways, a direct and an indirect. The former contribution is connected with the W_{nn} term (B-5) which gives the direct dependence of the phonon spectrum on the electronic state. Thus the energy needed for a given electronic excitation must include this change $\delta E_g^{(2)} = \sum_i n_i \delta \hbar\omega_i^{(2)}$. The indirect contribution is the self-energy of the electron-hole pair excitation derived in much the same way as in Chapter 4 for the reverse problem. The real part or shift is given by

$$\delta E_g^{(1)} = \sum_{\lambda \vec{q}s} |H_s(0 \rightarrow \lambda \vec{q})|^2 \left\{ \frac{n_{\vec{q}s}}{\hbar\omega - E_{\lambda \vec{q}} + \hbar\omega_{\vec{q}s}} + \frac{n_{\vec{q}s} + 1}{\hbar\omega - E_{\lambda \vec{q}} - \hbar\omega_{\vec{q}s}} \right\} \quad (5-12)$$

where the phonon occupation factors have been extracted from the squared matrix element for absorption and emission. The shift is evaluated at the gap frequency which is essentially $\hbar\omega = E_0$. A comparison with the total Fan term (5-7) and the direct second-order W_{nn} -term proves the practical identity of the static (free-energy) and dynamic (optical) energy gaps. In principle, there might be a slight difference because $\delta E_g^{(1)}$ in (5-12) is frequency dependent so that evaluation at $\hbar\omega = E_0$ (rather than at $\hbar\omega = E_0 + \delta E_g(\hbar\omega)$) does not give the exact result.

The above self-energy has an imaginary part also. This will be associated with the limited lifetime of the electronic excitation and shows up as broadening of the optical spectrum. We shall return to this part in the subsequent section.

In relation to the foregoing chapters we should like to mention that the formula (5-4) for the temperature dependence of the gap can in principle be checked experimentally. By neutron spectroscopy we can measure the complete phonon spectrum $\hbar\omega_1$, as well as its change $\delta(\hbar\omega_1)$ due to large doping by donors or acceptors. Apart from effects for small $|\bar{q}|$ (and intervalley phonons in relation to the conduction band) due to carrier degeneracy, $\delta(\hbar\omega_1)$ is independent of the carrier distribution. Thereby we can find the contributions to $\delta(\hbar\omega_1)$ from one hole and one electron at the appropriate band edges separately. However, we do not consider the procedure worth while in practice, but it illustrates the intimate connection between different manifestations of the electron-phonon interaction.

The temperature dependence of the band structure near the edges, i.e. the effective-mass parameters, represents an unsettled question. The above discussion of the phonon renormalisation of the band-edge energies applies to any excited state of the electronic system. Furthermore, the equivalence of the shifts for the two extreme ways of excitation, thermal and optical, supports the conjecture that the shift is generally independent of the method of excitation. It follows

that the temperature dependence of the general band structure arises from both thermal expansion and phonon interaction. There is no disagreement about that.

The principal energy gaps are usually fitted to experiment because first-principles calculations would be too uncertain. The effective-mass parameters can be related to these gaps by k·p theory (cf. eq. (2-7)). Similarly, we are unable to calculate the thermal shift of the band edges, but perhaps the change in the effective-mass parameters can be derived from k·p theory using the experimental information on band-edge shifts.

Let us for the purpose of illustration apply eq. (2-7) to a simple edge $|1\rangle$ at $\bar{k}=0$, where the inverse effective mass becomes

$$\frac{m}{m_1^*} = 1 + \frac{2}{m} \sum_{n \neq 1} \frac{|\langle 1 | p_x | n \rangle|^2}{E_1 - E_n(0)} \quad (5-13)$$

The question is then whether the temperature dependence of m_1^* is described by this formula through the variations of the energy gap. We shall find that this is not the case in the sense that the energy gaps will not be the experimental ones. The change in the p matrix element is generally agreed to be negligible (Lawaetz 1972).

Ehrenreich (1957) claimed in a footnote to have shown elsewhere (unpublished) that only the effect of thermal expansion on the gap should be taken into account in (5-13). This statement has had tremendous influence on all subsequent applications, and a negation by Ravich (1965), showing that the full gap shift should enter, went unnoticed. Experimental evidence on III-V compounds by Stradling and Wood (1970) and Koteles and Datars (1974) indicates that Ehrenreich's principle is not correct, but that Ravich's result is not the answer either.

In the subsequent analysis we study a very simple and idealised model of the problem, and the result is in qualitative agreement with experiment.

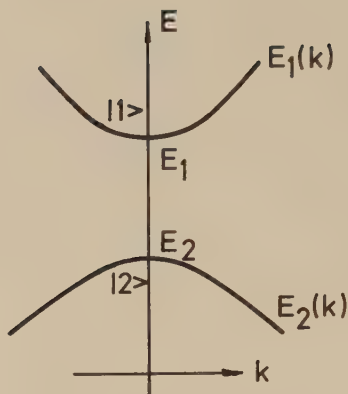


Figure 5.1. Simple two-band model of the unrenormalised one-electron band structure.

We assume a two-band model as shown in Fig. 5.1 and disregard all influence from more distant bands. (These could easily be included, but would just complicate the expressions). Conventional $k \cdot p$ perturbation as outlined in Chapter 2 gives the following expression for the conduction-band dispersion relation in the parabolic region

$$E_1(k) = E_1 + \frac{\hbar^2 k^2}{2m} + \frac{\hbar^2}{m^2} \frac{|\langle 1 | \bar{k} \cdot \bar{p} | 2 \rangle|^2}{E_1 - E_2} \quad (5-14)$$

The energy change due to small changes in E_1 and E_2 is then

$$\begin{aligned} \delta E_1(k) &= \delta E_1 - \frac{\hbar^2}{m^2} \frac{|\langle 1 | \bar{k} \cdot \bar{p} | 2 \rangle|^2}{(E_1 - E_2)^2} \delta(E_1 - E_2) \\ &= (1 - \kappa^2) \delta E_1 + \kappa^2 \delta E_2 \end{aligned} \quad (5-15)$$

with the $k \cdot p$ band-mixing parameter

$$\kappa^2 = \left| \frac{\hbar}{m} \frac{\langle 1 | \vec{k} \cdot \vec{p} | 2 \rangle}{E_1 - E_2} \right|^2 \quad (5-16)$$

If the shift δE_n of the band edge E_n is a property of the wave function $|n\rangle$ and independent of the actual energy, eq. (5-15) yields the effect of complete renormalisation, i.e. the band structure follows $k \cdot p$ theory with the adjusted gap energy. This property is obviously relevant for the contributions to δE_n from thermal expansion and direct second-order phonon interaction. However, the indirect (self-energy) contribution $\delta E^{(1)}$ (5-12) depends on energy ($\hbar\omega$ in eq. (5-12)) and may thus behave differently.

For reasons of simplicity we neglect the phonon frequencies in the denominators of (5-12), and so in the present notation

$$\delta E_n^{(1)}(E) = \int d^3k \frac{M_n}{E - E_n(k)} \quad (5-17)$$

where we assume that the quantity M_n is independent of $\vec{k}$, a relevant idealisation for nonpolar interactions. The above integral does not converge very well for large k (related to the importance of short-wavelength phonons), but suppose we know its value for $E = E_n$:

$$\delta E_n^{(1)}(E) = \delta E_n^{(1)}(E_n) + \int d^3k M_n \frac{E_n - E}{[E - E_n(k)]^2 [E_n - E_n(k)]} \quad (5-18)$$

The remaining integral shows much better convergence, and the result for a parabolic band

$$E_n(k) = E_n + A_n k^2 \quad (5-19)$$

(extending to infinity) is for $n=1$

$$\delta E_1^{(1)}(E) = \delta E_1^{(1)}(E_1) + \begin{cases} 0 & \text{for } E \geq E_1 \\ \Delta_1(E) & \text{for } E < E_1 \end{cases} \quad (5-20)$$

and for $n=2$ (while shifting E to conform with Fig. 5.1)

$$\delta E_2^{(1)}(E) = \delta E_2^{(1)}(E_2) + \begin{cases} 0 & \text{for } E \leq E_2 \\ \Delta_2(E) & \text{for } E > E_2 \end{cases} \quad (5-21)$$

with

$$\Delta_1(E) = 2\pi^2 M_1 A_1^{-\frac{3}{2}} (E_1 - E)^{\frac{1}{2}} \quad (5-22)$$

$$\Delta_2(E) = -2\pi^2 M_2 |A_2|^{-\frac{3}{2}} (E - E_2)^{\frac{1}{2}}$$

Insertion in (5-15), where $E \approx E_1$, gives approximately for the conduction-band shift:

$$\begin{aligned} \delta E_1^{(1)}(k) &= (1 - \kappa^2) \delta E_1^{(1)}(E_1) + \kappa^2 \delta E_2^{(1)}(E_2) \\ &\quad - \kappa^2 2\pi^2 M_2 |A_2|^{-\frac{3}{2}} (E_1 - E_2)^{\frac{1}{2}} \end{aligned} \quad (5-23)$$

The last term is the correction to the "fully" renormalised band. We observe that the band is still parabolic ($\kappa^2 \propto k^2$), but that the effective mass is larger than obtained from $k \cdot p$ theory (Ravich's). On the other hand, the Ehrenreich procedure corresponds to neglecting all terms with κ^2 in (5-23), so that the correct mass is in general smaller than Ehrenreich's. This is in qualitative agreement with the experimental data by Koteles and Datars (1974) for InSb.

The final result of this simplified model may be expressed in the form of an effective gap to be used in $k \cdot p$ theory.

From (5-14), (5-15), and (5-23) we obtain for the conduction band

$$\delta \left(\frac{\hbar^2 k^2}{2m_1^*} \right) = -\kappa^2 (\delta E_g^{\text{obs}} + 2\pi^2 M_2 |A_2|^{-\frac{3}{2}} E_g^{\frac{1}{2}}) \quad (5-24)$$

so that the relevant correction to the observed energy gap is

$$E_g^{\text{eff}} - E_g^{\text{obs}} = 2\pi^2 M_2 |A_2|^{-\frac{3}{2}} E_g^{\frac{1}{2}} \quad (5-25)$$

Thus if the last term is at all significant, $k \cdot p$ theory with observed energy gaps is inaccurate, even at $T = 0$.

An estimate of the order of magnitude can be made in the same spirit as (5-10) at $T = 0$:

$$2\pi^2 M_2 |A_2|^{-\frac{3}{2}} E_g^{\frac{1}{2}} \approx \frac{3}{\pi\sqrt{2}} \frac{d_o^2 m_2^{*3/2} E_g^{\frac{1}{2}}}{\hbar^2 \rho \omega a_c^2} \quad (5-26)$$

where m_2^* is a typical hole effective mass. Insertion of Ge-parameters ($d_o = 27$ eV, $m_2^* \approx 0.3$ m) yields 20 meV, which should be compared with the total shift $\delta E_g^{\text{obs}}(T=0) \approx -160$ meV

We conclude that the correction is significant whenever the thermal variation of the gap has any influence on the effective-mass parameters. Considering the present experimental accuracy of determining band gaps (~ 1 meV) and effective masses of simple bands ($\sim 0.5\%$), this is the rule rather than the exception. A more detailed model of the phonon contribution will be needed, but is considered feasible at least for small-gap materials like InAs and InSb.

It may be particularly interesting to reconsider the interpretation of interband magneto-optical spectra because this involves the energy gap and the effective-mass parameters in various combinations. The parameters giving the best fits are usually somewhat at variance with other evidence and have led to the proposal of a fundamental difference between inter-

band and intraband quantities (Pidgeon and Groves (1969), Groves et al. (1970)). We believe that proper consideration of the phonon contribution may resolve the problem and make the results of this type of experiment more reliable.

We finally remark that we have treated only the nonpolar electron-phonon interaction. Polaron features ought to be included as well, but their effects are generally much smaller in the materials investigated here.

5.2. Effect of phonons on the hole energy spectrum

As mentioned above, the general self-energy contribution to the band structure cannot be calculated because of the vast range of phonon modes involved. However, certain features involving only a limited region of phonon wave-vector space are tractable. This concerns in particular the imaginary part of the self-energy which shows up as lifetime broadening, but also certain differences in the real part or shift can be computed. Of the latter category we mention the correction to the effective-mass energy gap discussed in the previous section and the phonon contribution to the spin-orbit splitting to be treated below. Lifetime broadening can be computed because both momentum and energy conservation are obeyed. Examples are the phonon structure in the direct and indirect absorption edges and ordinary broadening of direct edges. This second feature is the main subject of the present section because its analysis leads to a supplementary determination of interaction parameters for holes and optic phonons.

A fundamental structure in the optical spectra of semiconductors is the E_0 edge and its spin-orbit split-off partner $E_0 + \Delta_0$. Their relation to the energy-band structure is depicted in Fig. 5.2. The excitation of electron-hole pairs occurs in the form of excitons due to the Coulomb interaction between electron and hole. The resulting hydrogenic energy spectrum shows up in absorption in a suitably broadened version as sketched on Fig. 5.3 for GaP. The analysis of

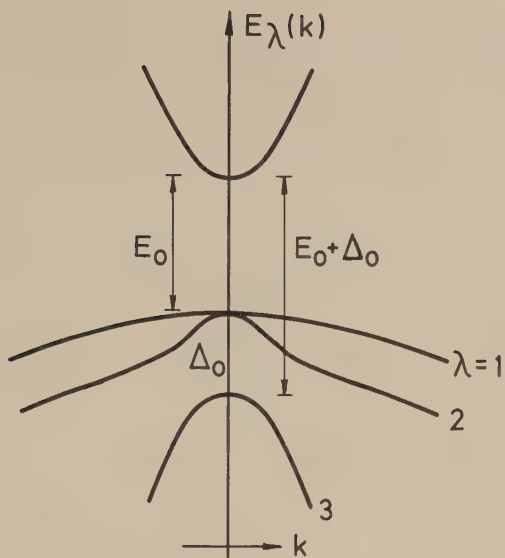


Figure 5.2. Electronic energy-band structure near $k=0$ showing the thresholds for the E_0 and $E_0 + \Delta_0$ transitions.

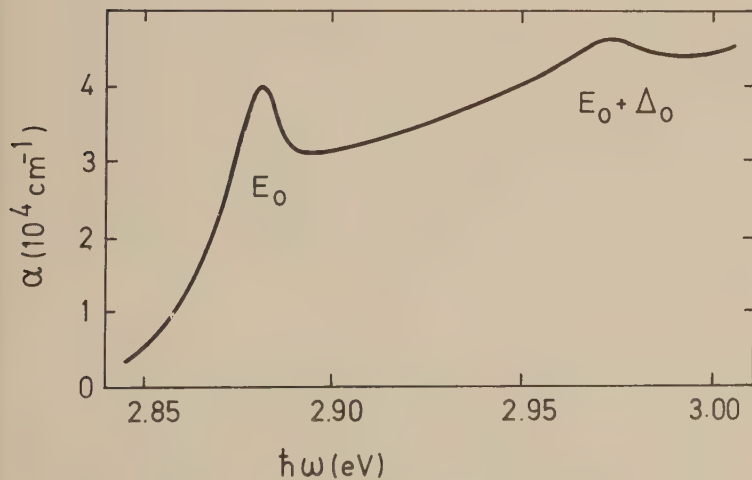


Figure 5.3. The direct absorption edge of GaP at 25K showing the broadened excitonic structure at E_0 and $E_0 + \Delta_0$, see Sell and Lawaetz (1971). α is the ordinary absorption coefficient.

the spectrum in terms of simple Lorentzian broadening is described by Sell and Lawaetz (1971) and results in broadening parameters Γ for the two edges. Similar techniques can be applied to other types of experimental spectra (e.g. piezo-, electro- and magnetorelectance), so that data exist for many semiconductors.

For reasonably pure crystals the origin of the exciton broadening is phonon scattering. Provided that the energy of the involved phonon is much larger than the exciton binding energy, we can neglect excitonic effects and consider the electron and the hole separately. Thus the broadening Γ is the sum of electron and hole contributions, but only holes contribute to the difference $\Gamma(E_0 + \Delta_0) - \Gamma(E_0)$. For direct semiconductors at low temperature $\Gamma(E_0)$ is vanishingly small because phonon emission is energetically impossible and no phonons are present to be absorbed. However, $\Gamma(E_0)$ can be quite appreciable in indirect materials since the electron can scatter by phonon emission. These complications are avoided by considering the above difference.

The original experimental investigation of $\Gamma(E_0)$ and $\Gamma(E_0 + \Delta_0)$ goes back to Hobden (1962) and McLean and Paige (1963) and was based on absorption in Ge. Since then numerous papers have studied the E_0 and $E_0 + \Delta_0$ structures by refined techniques, but little has been published because broadening is usually considered a nuisance. Sell (unpublished) has collected and analysed the data by personal contact with the authors, and the results are shown in Table 5.1 with due reference to papers containing the principal data by the relevant people.

The theoretical interpretation of the low temperature data is based on the lifetime broadening of the free hole at the edge of the spin-orbit split-off band due to emission of optic phonons. The created hole decays by phonon scattering into the light- and heavy-hole band states as illustrated in Fig. 5.4. Note that the hole generated by the E_0 process cannot decay, so that its contribution to $\Gamma(E_0)$ is vanishing.

Table 5.1. Experimental evidence on the broadening difference $\Gamma(E_O + \Delta_O) - \Gamma(E_O)$. The data were collected by D.D. Sell and refer to low temperature.

Material	Method	$\Gamma(E_O + \Delta_O) - \Gamma(E_O)$ (meV)
Ge	magnetorefl. ^a	6
	electrorefl. ^b	6
GaP	absorption ^c	6
GaAs	reflectance ^d	10
	magnetorefl. ^e	11
	electrorefl. ^f	6±2
GaSb	magnetorefl. ^g	8
InP	electrorefl. ^h	10
ZnSe	reflectance ⁱ	18
ZnTe	reflectance ⁱ	16
CdTe	reflectance ⁱ	16

^aAggarwal (1970)

^bFischer (1970)

^cSell and Lawaetz (1971) based on data by Dean et al. (1967).

^dSell and Stokowski (1970)

^eReine et al. (1970a)

^fAspnes and Studna (1973)

^gReine et al. (1970b)

^hD.E. Aspnes and J.E. Rowe (unpubl.)

ⁱD.D. Sell (unpubl.)

The neglect of the internal motion of the exciton is considered a very good approximation as long as the exciton binding energy E_B is small compared with the spin-orbit splitting Δ_O and the optic phonon energy $\hbar\omega$. If $E_B \ll \Delta_O$,

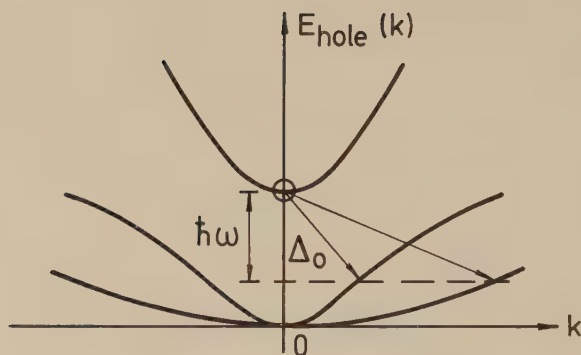


Figure 5.4. Hole energy spectrum showing the decay processes from the split-off state at $k=0$ through emission of optic phonons with energy $\hbar\omega$.

the $E_0 + \Delta_0$ exciton will couple to the background continuum associated with the E_0 structure as a consequence of the same features which give rise to nonparabolicity (Baldereschi and Lipari 1971). These authors identified this coupling with an intrinsic broadening, but it should rather give rise to a spectral structure of the Fano-type. The q -parameters (as estimated from their results) are generally large for the materials in question, and so this effect is negligible (except perhaps for ZnS, but this is not interesting here as we explain below). A similar effect can be caused by exchange interaction (Onodera 1971).

The condition $\hbar\omega \gg E_B$ should hold because otherwise the optic-phonon scattering is not a free-hole process, but will be affected by the specific exciton properties. Such effects are expected to show up as a broadening depending strongly on excitation energy, and there is no evidence for that. Of course, if the sum of binding energy and

optic-phonon energy is close to or exceeds the spin-orbit splitting, the density of final states will be reflected in a frequency-dependent broadening and the magnitude will be small. Examples of such "uninteresting" materials are Si, where $\hbar\omega = 65$ meV and $\Delta_O = 44$ meV, and ZnS, for which $\Delta_O = 70$ meV (Table 2.1), $E_B \approx 29$ meV (Baldereschi and Lipari 1971), and $\hbar\omega \approx 40$ meV (Burstein et al. 1967). The ZnS spectrum obtained by Bir et al. (1970) clearly displays the absence of $E_O + \Delta_O$ broadening, at least for the ground-state $E_O + \Delta_O$ exciton.

Our model also neglects scattering by acoustic phonons. This is obviously allowed at very low temperatures, but at room temperature the number of relevant phonons is appreciable, and data for GaAs (Sell and Stokowski 1970) may be an indication that this mechanism should be taken into account if we tried to explain the temperature dependence of the broadening.

The calculation of the lifetime broadening Γ_3 of the split-off hole is based on the golden rule formula (assuming unit-volume):

$$\Gamma_3 = 3\pi \sum_{\lambda \bar{k}} |H_{3\lambda}(0, \bar{k})|^2 \delta(\Delta_O - E_\lambda(\bar{k}) - \hbar\omega) \quad (5-27)$$

where the factor of 3 results from summation over the three polarisation directions of the optic phonon. In polar materials, the optic phonon polarisations are not degenerate, but we take a suitable average because the energy dependence in (5-27) is very weak. The correspondingly averaged, squared matrix element is given in (B-45)

$$|H_{\lambda\lambda}, (0, \bar{k})|^2 = \frac{\hbar}{2\rho\omega a_c^2} \frac{(m_1 + m_2)^2}{4m_1 m_2} \times \{g_{\lambda\lambda}^{n1}, d_O^2 + g_{\lambda\lambda}^{n2}, a_1 d_O + g_{\lambda\lambda}^{n3}, a_1^2 + g_{\lambda\lambda}^p, a_p^2\} \quad (5-28)$$

where the g -factors depending on E_{λ} and $\hat{k}$ are specified in Appendix B, and d_o , a_1 , and a_p are coupling parameters. d_o is the optic deformation potential, a_1 is a nonpolar multipole parameter, and a_p describes the strength of the polar-optic coupling. Expression (5-28) is valid only for spontaneous phonon emission and should be multiplied by suitable phonon occupation factors when used in connection with temperature dependence.

The energy-conserving delta function in (5-27) refers only to continuous variables, and so we transform the sum over $\bar{k}$ into integrals (cf. eqs. (2-29) through (2-35))

$$\Gamma_3 = \frac{3m^{3/2}\Delta_o^{\frac{1}{2}}}{2\sqrt{2}\pi\rho\omega a_c\hbar^2} \frac{(m_1+m_2)^2}{4m_1m_2} \frac{1}{4\pi} \int d^2\hat{k} \left(1 - \frac{\hbar\omega}{\Delta_o}\right)^{\frac{1}{2}} \times \sum_{\lambda=1}^2 \tilde{D}_{\lambda}(\hat{k}, \Delta_o - \hbar\omega) \{g_{3\lambda}^{n1}d_o^2 + g_{3\lambda}^{n2}a_1^2d_o + g_{3\lambda}^{n3}a_1^2 + g_{3\lambda}^pa_p^2\} \quad (5-29)$$

where $\tilde{D}_{\lambda}(\hat{k}, E)$ is the density-of-states factor given in eq. (A-17). It remains to carry out the angular integration which must be performed numerically.

In the nonparabolic treatment of the valence-band structure in Chapters 3 and 4, we considered only the nonparabolicity arising from spin-orbit splitting effects, i.e. effects within the manifold of Γ_{25}' basis states. However, as discussed in Sec. 2.1, there is also a nonparabolicity due to the proximity of the Γ_2' conduction-band level. This was neglected in connection with the free-hole effects on the phonon spectrum because the calculated effects were relative to the hole concentration, and so the influence of an increased density-of-states should be small. In the present situation of broadening, the computed effect is absolute, and the additional nonparabolicity will thus be more important.

In practice, this nonparabolicity is approximately accounted for by the Löwdin method as discussed in connection with

eq. (2-16). The procedure presupposes that the band structure is solved for k^2 for a specified direction $\hat{k}$ and energy E , but this is exactly what is required in eq. (5-29).

The necessary band parameters were shown in Table 2.1, and additional quantities in (5-29) are listed in Table 5.2 including the value of the total prefactor

$$f_{\Gamma} = \frac{3m^{3/2}\Delta_O^{\frac{1}{2}}}{2\sqrt{2}\pi\rho\omega_a^2\hbar^2} \frac{(m_1+m_2)^2}{4m_1m_2} \quad (5-30)$$

and a_p . The computational results will be shown as the coefficients ξ_i in the quadratic form derived from (5-29)

$$\Gamma_3 = \xi_1 d_O^2 + \xi_2 a_1 d_O + \xi_3 a_1^2 + \xi_p a_p^2 \quad (5-31)$$

Table 5.3 contains these results together with values of $(\Gamma_{3\text{exp}} - \xi_p a_p^2)$ which should correspond to the nonpolar contribution. $\Gamma_{3\text{exp}}$ is identical to $\Gamma(E_O + \Delta_O) - \Gamma(E_O)$ shown in Table 5.1.

Now, if d_O has been determined by other means like the method described in Chapter 4, we can finally determine the possible values of a_1 , the multipole parameter. Unfortunately, the coefficients ξ_2 and ξ_3 of the multipole terms in (5-31) are much smaller than ξ_1 , and so the multipole contribution is detectable only if $|a_1| \gg |d_O|$. This is not likely. Previous estimates of a_1 ($=C_O a_C$) yield 8.6 eV for Ge (Lawaetz 1969) (Pindor (1972) finds 33 eV using a different screening of the multipoles) and less than 10 eV for Si (Vogl et al. 1976). Consequently, the best interpretation is obtained by neglecting multipoles altogether. It is then possible to determine d_O from the broadening data, and the values are listed in Table 5.3.

Inspection of the values of this optic deformation potential shows that it is relatively small for the II-VI compounds, but otherwise there are no obvious trends. This is because

Table 5.2. Lattice data to be used for the calculation of broadening etc. The unusual unit for f_T arises because Γ is in meV and the deformation potential in eV.

Material	a_c (Å)	ρ (gcm ⁻³)	m_l^a	m_2^a	$\hbar\omega$ (meV) ^b	$b_{r\infty}$	b_{rs}	a_p (eV)	f_T (10 ⁵ eV) ⁻¹
Ge	5.66	5.33	73	73	37	16.0	16.0	0.	0.961
Si	5.43	2.33	28	28	65	12.0	12.0	0.	0.525
AlSb	6.12	4.33	27	122	41	10.2	12.0	19.2	2.275
Gap	5.43	4.18	70	31	47	9.1	10.7	69.8	0.633
GaAs	5.63	5.40	70	75	36	10.9	12.9	30.4	1.059
GaSb	6.10	5.78	70	122	30	14.4	15.7	11.4	1.641
InP	5.85	4.85	115	31	41	9.6	12.6	59.6	0.885
InAs	6.02	5.79	115	75	29	12.3	15.1	25.8	1.185
InSb	6.46	5.85	115	122	24	15.7	17.9	11.6	1.719
ZnS	5.40	4.10	65	32	40	5.14	8.00	129.9	0.699
ZnSe	5.65	5.33	65	79	29	5.90	8.33	40.2	1.500
ZnTe	6.08	5.70	65	128	24	7.28	9.86	20.6	2.373
CdTe	6.47	5.90	112	128	19	7.13	10.20	20.2	2.283

^a atomic units.

^b Burstein et al. (1967); the values of $\hbar\omega$ are averaged over longitudinal and transverse modes.

Table 5.3. Calculated values of coefficients in eq. (5-31). ξ -values are in $(10^5 \text{ ev})^{-1}$, Γ 's in meV, and d_0 in ev.

Material	ξ_1	ξ_2	ξ_3	ξ_p	$\xi_p a^2$ p p	$\Gamma_{3\text{exp}}$	$\Gamma_{3\text{exp}}^{-\xi} a^2$ p p	$d_0 (a_1=0)$
Ge	0.398	-0.063	0.009	0.143	0	6	6.0	39.
AlSb	1.913	-0.218	0.029	0.311	1.15	-	-	-
GaP	0.231	-0.007	0.000	0.016	0.78	6	5.2	47.
GaAs	0.511	-0.054	0.008	0.160	1.48	10 ^a	8.5	41.
GaSb	0.738	-0.100	0.015	0.231	0.30	8	7.7	32.
InP	0.496	-0.035	0.004	0.113	4.01	10	6.0	35.
InAs	0.565	-0.066	0.011	0.244	1.62	-	-	-
InSb	0.780	-0.111	0.018	0.297	0.34	-	-	-
ZnSb	1.749	-0.150	0.025	0.315	5.09	18	12.9	27.
ZnTe	2.654	-0.280	0.041	0.414	1.76	16	14.2	23.
CdTe	2.888	-0.325	0.052	0.515	2.10	16	13.9	22.

^a Only the most likely value shown.

d_0 as a matrix element in the valence-band basis is affected by the lattice constant, the ionic admixture of conduction-band Γ_{15} states, a possible explicit ionic contribution, and spin-orbit effects, and they are not easily sorted out in any detail. We shall deal only with the spin-orbit effects in Ge, which may cause the apparent discrepancy between the present value of $d_0 \approx 39$ eV and that $d_0 \approx 27$ eV determined in Chapter 4 from the shift of the optic-phonon resonance.

However, before entering these details we shall mention that additional broadening mechanisms have been considered (which might reduce the fitted value of 39 eV). The most prominent candidate is two-phonon processes involving the consecutive emission of two optic phonons. This investigation is the subject of a short account presented elsewhere (Lawaetz et al. 1974), and since the result is essentially negative, we shall not go into more detail here.

So far we have based our considerations of matrix elements in the sixfold valence-band basis on the form and symmetry of the extended Shockley matrix typefied in eqs. (2-12) and (2-13) or eqs. (A-48) and (A-49). This type of matrix contains only 3 parameters (a, b, and d type) because spin-orbit effects are included only to the extent of reorganising the basis. Actually, we have explicit spin-orbit contributions, and the most general form of the 6×6 matrix is rather given by (A-37) corresponding to 6 parameters. In the case of d-like elements we find (following Hensel and Suzuki (1974)) one d_u in the elements of the upper left 4×4 section of the matrix, no d in the lower right 2×2 section, and one d_w in the remaining 2×4 sections. Thus d_u appears in $\Gamma_8^+ - \Gamma_8^+$ interactions (heavy and light holes) whereas d_w enters $\Gamma_8^+ - \Gamma_6^+$ interactions (split-off holes to heavy and light). According to Hensel and Suzuki (1974), the acoustic deformation potential can be written as

$$d_u = d + d', \quad d_w = d - \frac{1}{2}d' \quad (5-32)$$

where d' is the spin-orbit contribution. For Ge, they find the values $d = 3.6$ eV and $d' = 0.8$ eV.

A similar spin-orbit contribution must be present in the case of the optic deformation potential d_o . It is evident that the $(E_o + \Delta_o)$ -broadening involves only d_{ow} , whereas the phonon shift γ in chapter 4 is dominated by d_{ou} because most of the contributions arise from transitions within the Γ_8^+ band-edge manifold. Thus our arguments suggest the identifications

$$\begin{aligned} d_{ou} &= d_o + d' = 27 \text{ eV} \\ d_{ow} &= d_o - \frac{1}{2}d' = 39 \text{ eV} \end{aligned} \tag{5-33}$$

and so $d_o = 35$ eV and $d'_o = -8$ eV. Apart from the sign, the ratio d'_o/d_o is of the same magnitude as d'/d . We conclude that this is a very likely explanation of the otherwise spectacular difference in the values of d_o derived from the two experiments.

There exists a third determination of d_o in Ge based on low-field hole transport (Lawaetz 1968). This d_o belongs to the Γ_8^+ manifold, and the value is $d_{ou} = 40$ eV. It is now known that nonparabolicity is much stronger than assumed in that work, in particular for the heavy-hole band in the (110) direction. Furthermore, multipole scattering was not considered, and several other problems were left unsolved. Consequently, the above value is probably too large and cannot be used to check our conclusions.

Above, we have studied the lifetime broadening Γ of holes at the band edges at $k = 0$. Γ is essentially the imaginary part of the hole self-energy, and so it is natural to extend the investigations to cover the real part δ also. Thus $\delta_3 - \delta_o$ is the optic phonon contribution to the spin-orbit splitting at $T = 0$, and by analogy with (5-29) it is given by

$$\delta_3 - \delta_0 = f_T \frac{1}{\pi} \int_{(0)}^{\infty} d\left(\frac{E}{\Delta_0}\right) \left(\frac{E}{\Delta_0}\right)^{\frac{1}{2}} \sum_{\lambda=1}^3 \frac{\tilde{r}}{4\pi} \int d^2 \hat{k} D_{\lambda}(\hat{k}, E) \left\{ \right\} \quad (5-34)$$

$$\left\{ \right\} = \left\{ \left(\frac{g_{3\lambda}^{n1}}{1 - \frac{\hbar\omega}{\Delta_0} - \frac{E}{\Delta_0}} + \frac{g_{0\lambda}^{n1}}{\frac{\hbar\omega}{\Delta_0} + \frac{E}{\Delta_0}} \right) d_0^2 + \dots \right\} \quad (5-35)$$

including similar terms with $a_1 d_0$, a_1^2 , and a_p^2 . The individual nonpolar contributions δ_3^n and δ_0^n exhibit very bad convergence of the integral, but the difference is reasonably well defined. Convergence is better for the polar terms δ_3^p and δ_0^p , and $-\delta_0^p$ is in fact the hole-polaron binding energy at Γ_8^+ (and $T = 0$). However, only $\delta_3^p - \delta_0^p$ is found to converge so rapidly that it depends entirely on the reliably known part of the valence-band structure. The others, i.e. $\delta_3^n - \delta_0^n$ and $-\delta_0^p$, reach too far out in the Brillouin zone so that their uncertainty is estimated to be 10-20%.

The phonon contribution to the spin-orbit coupling is characterised by the coefficients η in the following expression:

$$\delta_3 - \delta_0 = \eta_1 d_0^2 + \eta_2 a_1 d_0 + \eta_3 a_1^2 + \eta_p a_p^2 \quad (5-36)$$

These coefficients are shown in Table 5.4. Again the coefficients η_2 and η_3 of the multipole terms are so small that this contribution can be neglected. The table also shows resulting values of $\delta_3 - \delta_0$ deduced by insertion of values of d_0 and a_p . Since d_0 may contain appreciable spin-orbit contributions where the spin-orbit splitting is large, the results are most reliable for materials with small spin-orbit splittings like Si, GaP, and ZnS. It is therefore gratifying that the effect is greatest in GaP and ZnS where the

Table 5.4. η - and ζ -coefficients (in $(10^5 \text{ eV})^{-1}$) of the real part of the hole self-energy and nonpolar (η_p), polar (p), and total (t) phonon contribution $\delta_{3-\delta_O}^p$ (mev) to the spin-orbit splitting. Values of d_O (eV) are either from Table 5.3, Chapter 4 (Si) or assumed (*). $-\delta_O^p$ (mev) is the polaron binding energy at the valence-band edge.

Material	η_1	η_2	η_3	η_p	ζ_p	$-\delta_O^p$	d_O	(np)	(p)	(t)
Ge	-0.258	0.045	-0.007	0.058	0.319	0.	39	-3.9	0.	-3.9
Si	-0.239	0.031	-0.003	-0.006	0.073	0.	27	-1.74	0.	-1.74
AlSb	-1.005	0.115	-0.014	0.189	1.303	4.8	20*	-4.0	0.70	-3.3
GaP	-0.330	0.027	-0.003	-0.021	0.138	6.7	47	-7.3	-1.02	-8.3
GaAs	-0.294	0.034	-0.005	0.068	0.433	4.0	41	-4.9	0.63	-4.3
GaSb	-0.399	0.051	-0.007	0.143	0.765	0.99	32	-4.1	0.186	-3.9
InP	-0.434	0.049	-0.007	-0.025	0.261	9.3	35	-5.3	-0.89	-6.2
InAs	-0.315	0.037	-0.006	0.134	0.490	3.3	32*	-3.2	0.89	-2.3
InSb	-0.412	0.056	-0.008	0.189	0.762	1.03	29*	-3.5	0.25	-3.2
ZnS	-0.789	0.047	-0.006	-0.034	0.204	34.	35*	-9.7	-5.7	-15.4
ZnSe	-0.879	0.075	-0.011	0.184	0.949	15.3	27	-6.4	2.97	-3.4
ZnTe	-1.249	0.116	-0.014	0.292	1.667	7.1	23	-6.6	1.24	-5.4
CdTe	-1.358	0.134	-0.017	0.384	1.611	6.6	22	-6.6	1.57	-5.0

phonon contribution to the spin-orbit splitting amounts to 10-20%. Another more general result is that the nonpolar part is usually dominant and negative, i.e. the spin-orbit splitting is reduced by the optic phonons.

The theory of polarons in degenerate bands was sketched by Kahn (1968). Trebin and Rössler (1975) as well as Beni and Rice (1977) worked out the hole-polaron binding energy and mass correction for a spherical, parabolic two-band model of the valence-band edge. Our results cover only the binding energy

$$-\delta_{\text{O}}^{\text{P}} = \zeta_{\text{P}} a_{\text{P}}^2 \quad (5-37)$$

where $-\delta_{\text{O}}^{\text{P}}$ and ζ_{P} are listed in Table 5.4, but the calculation is not restricted by any severe approximations in the band structure. In fact, it is found that nonparabolicity is very important due to slow convergence in the heavy-hole band. The actual numbers show that perturbation theory is not valid for the II-VI compounds where the binding energy is comparable to the phonon energy.

It will be of considerable interest to extend the present calculations to $k \neq 0$ so that polaron contributions to the band parameters can be found and perhaps compared with experiments. The matrix-element factors $g_{\lambda\lambda}^{\text{P}}$, then have a much more complicated form and have to be worked out using the general results in Appendices A and B. This is outside the scope of the present work. However, we want to point out that the "nonpolaron" contribution to the mass renormalisation arising from the deformation-potential coupling (to the optic phonons) may be of comparable magnitude if not dominant, and so this ought to be included at the same time. This analysis of dressed holes will require extensive calculations.

6. CONCLUSION

The main theme of the present work has been the non-transport effects of the interaction between holes and phonons. By a detailed analysis of resonance shifts and broadenings we have determined a number of parameters describing the interaction: the acoustic deformation potential d and the optic deformation potential b_o . The parameter d could also have been deduced by the present methods, but it was not considered worth while because this information is more or less available already. An attempt to determine the quadrupole parameter a_1 has failed since the contribution from multipoles to the studied effects turned out to be negligible. On the other hand, our results for Ge indicate appreciable direct spin-orbit contributions to d_o . The determined parameters are summarised in Table 6.1. In principle, the

Table 6.1. Summary of fitted deformation potentials. The difference between d_{ou} and d_{ow} is discussed in Sec. 5.2. The value of d is essentially of the d_u type.

Material	d (eV)	d_{ou} (eV)	d_{ow} (eV)
Ge	4.4 ^a	27	39
Si	4.6	27	
GaP			47
GaAs	5.3 ^a		41
GaSb	4.4 ^a		32
InP			35
ZnSe			27
ZnTe			23
CdTe			22

^aBased on rather incomplete experimental data.

present methods of deriving deformation-potential constants from shift and broadening of phonon resonances have the advantage that the hole concentration and thus the effects can be varied in a controlled way over several decades.

An important feature in the theory leading to these results is an accurate treatment of the nonparabolic hole-band structure, not only the energy versus wave vector dispersion relation, but also its influence on the matrix elements for intervalence-band transitions. The resulting expressions for the squared matrix elements (Appendix A) can be useful for other purposes, e.g. theories of hole transport properties with phonon and impurity scattering and evaluation of the free-hole dielectric function $\epsilon(\omega, \vec{q})$.

Nature does not follow our ideal model in all detail. The large concentration of acceptors needed to produce the desired number of holes distorts the hole energy spectrum, the main effect here being the nonconservation of hole $\vec{k}$ -vector. This flaw is tentatively remedied for Ge by averaging the $\vec{q}$ -dependent phonon self-energy $\tilde{z}_p(\omega, \vec{q})$ over a region in $\vec{q}$ -space of the order of a reciprocal Bohr radius of the acceptor, and the results represent a definite improvement in the comparison with experimental data. Although not relevant in the above context, the calculations of $\tilde{z}_p(\omega, \vec{q})$ versus $\vec{q}$ reveal an unexpected richness of structure associated with the anisotropic hole-energy surfaces. Similar features should be present in the free-hole dielectric function.

The present methods based on long-wavelength optic phonon renormalisation can be extended to acceptor-doped III-V compounds in order to fill out empty spaces in the column d_{ou} in Table 6.1. However, in these polar materials the nonzero LO-TO phonon splitting is changed directly by free-hole screening, and so this plasmon complication must be included also. There are no experimental data available.

The restriction to long-wavelength phonons is set by the limits of Raman scattering (and ultrasonic techniques in the acoustic region). In addition the specific enhancement

effects in $\delta\omega/\omega$ show up only when the virtual hole (or electron) transitions are nearly real, i.e. under resonance conditions. This normally occurs only for small phonon wave vectors $|\vec{q}|$. However, the intervalley phonons in the many-valley conduction-band structure also satisfy this condition. If shifts and broadenings of these phonons can be detected by neutron spectrometry, we may have another interesting case where relevant coupling parameters can be derived by an independent method.

De Cerdeira (1973) sketched a theory for this situation, but we have been unable to follow it. Our picture is somewhat different: If the interaction matrix elements are known, we shift one valley by adding the wave vector $\vec{q}$ of the phonon in question and subsequently calculate the complex phonon self-energy with vertical transitions in the combined, overlapping bands as illustrated in Fig. 6.1. Compared with the valence-band situation we have somewhat simpler band

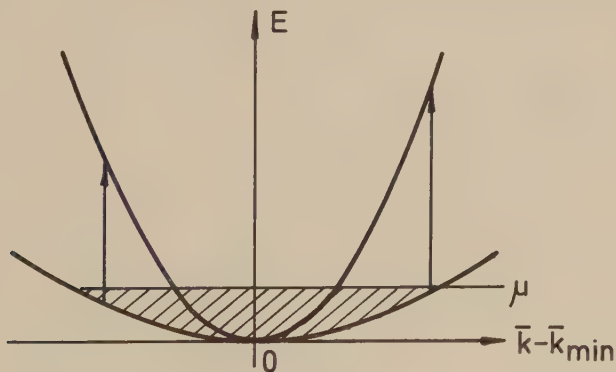


Figure 6.1. The combined (shifted-valley) band structure for f-scattering between perpendicular valleys in Si. In this example $\vec{q} = \vec{Q}$, the wave vector connecting the valley minima λ and λ' .

structures here, and the matrix elements are independent of $\bar{k}$ to a very good approximation (provided that they are nonzero everywhere in the region of interest). The qualitative $\bar{q}$ -dependence of the phonon resonance shift and broadening is shown in Fig. 6.2 for a couple of relevant situations. The shown absence of effects for intravalley optic phonons in n-Ge ($\bar{q}=\bar{Q}=0$) is confirmed by experiments using Raman scattering (Cerdeira and Cardona 1972).

However, this may only be part of the story. Free-carrier screening of the matrix element should also be considered. Intervalley screening by free electrons may be a tractable problem, but a simple separation of the lattice background as shown in Appendix B.3 for the long-wavelength case may not be feasible for the short wavelengths here. Thus, the possible outcome of the above method may have very little relevance for intervalley scattering in ordinary much purer crystals. A careful analysis is obviously required.

As shown in Chapter 5, the influence of holes on the phonon spectrum is reciprocal in the sense that the same mechanisms govern the influence of phonons on the hole spectrum. Overall properties such as the band-edge shift cannot be calculated because phonons of all wave vectors contribute, but the phonon contribution to small changes is tractable with reasonable reliability. We have studied such contributions to the spin-orbit splitting because this is probably the simplest situation. The next step is then the modification of the hole dispersion relation by the nonpolar and polar interactions, i.e. the mass renormalisation. We emphasize that the nonpolar contribution is likely to be as important as the polar so that polarons in themselves may be of limited physical reality.

The main conclusion of the present work is that satisfactory quantitative agreement between fundamental theoretical models and corresponding experiments related to hole properties can only be achieved when the hole-band structure is treated in detail. Several of the effects studied here more or less

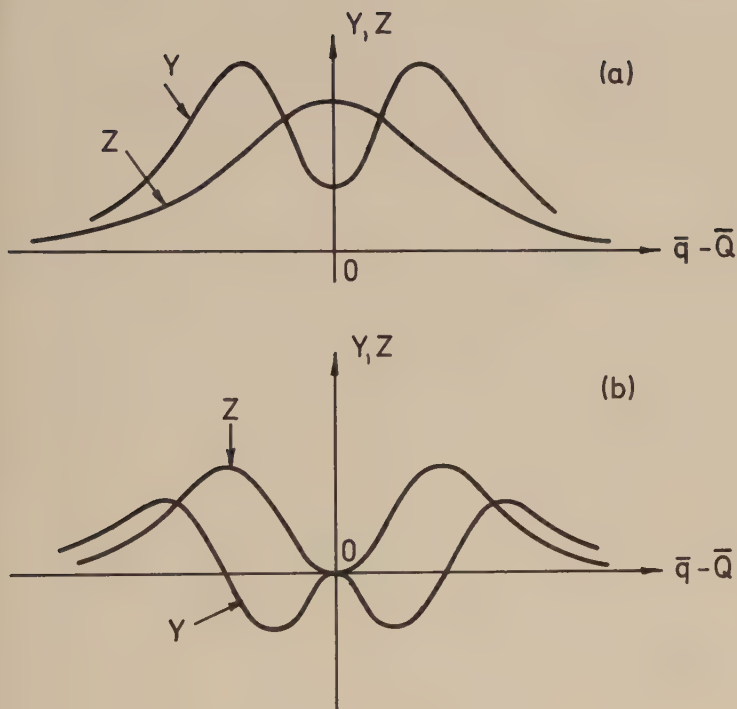


Figure 6.2. Illustration of $\bar{q}$ -dependence of normalised phonon shift Y and broadening Z for a fixed $\omega \neq 0$ in a many-valley band structure. The extension of the structure in $(\bar{q} - \bar{Q})$ -space is of the order of $2k_F$ in radius, a typical dimension of the Fermi surface in the valley. Case (a) applies to f-phonons in Si and intervalley phonons in Ge; case (b) applies to g-phonons in Si (parallel valleys) as well as to intravalley ($\bar{Q} = 0$) optic phonons in Ge. Case (b) is distinguished by complete degeneracy of the combined band structure for $\bar{q} = \bar{Q}$, the wave vector connecting the valley minima.

owe their existence to these details. It is therefore gratifying that this type of band structure occurs in a whole family of materials. This variety has not been fully exploited here because experimental data are not available. It is also obvious that many of the subjects can be further elaborated. It is hoped that the present work may have shown that holes are not really so tricky as they may appear to be.

Appendix A: Band structure and matrix elements in non-parabolic valence bands

A.1. Reduction of the band structure problem

The E vs. $\bar{k}$ relation for the three hole bands is found as the eigenvalues of the matrix $\bar{H}$ in eq. (2-12). As shown in (2-24) we shall express the solution in the form

$$\frac{\hbar^2 k^2}{2m} = E^* = E\beta_{\lambda}(E, \hat{k}) \quad (A-1)$$

β satisfies the following cubic equation (Asche and von Borzeskowski 1970)

$$c_1 \frac{E}{\Delta_0} \beta^3 + (A^2 - e^2) (1 - 3 \frac{E}{\Delta_0}) \beta^2 - A(2 - 3 \frac{E}{\Delta_0}) \beta + (1 - \frac{E}{\Delta_0}) = 0 \quad (A-2)$$

$$c_1 = (A+2B)(A-B)^2 - 3(A-B)(D^2 - 3B^2)\mu_4 + (D\sqrt{3} - 3B)^2(2\sqrt{3}D + 3B)\mu_6 \quad (A-3)$$

$$\mu_4 = \hat{k}_x^2 \hat{k}_y^2 + \hat{k}_y^2 \hat{k}_z^2 + \hat{k}_z^2 \hat{k}_x^2, \quad \mu_6 = \hat{k}_x^2 \hat{k}_y^2 \hat{k}_z^2 \quad (A-4)$$

Eq. (A-2) can be formally simplified by introducing

$$\alpha = A - \frac{1}{\beta} = A - \frac{E}{E^*} \quad (A-5)$$

$$\tilde{\alpha} = \frac{\Delta_0}{E^*} \quad (A-6)$$

so that the equation reads

$$\alpha^3 - 3\tilde{e}^2\alpha + c_0 + \tilde{\alpha}(\alpha^2 - e^2) = 0 \quad (A-7)$$

with (as in (2-21))

$$e^2 = \gamma_1 + \gamma_2 = B^2(1 - 3\mu_4) + D^2\mu_4 \quad (A-8)$$

$$\begin{aligned} c_0 &= c_1 (A = 0) \\ &= B^3 (2-9\mu_4 + 27\mu_6) + 3BD^2 (\mu_4 - 9\mu_6) + 6\sqrt{3}D^3 \mu_6 \end{aligned} \quad (A-9)$$

Eq. (A-7) is well suited for the solution E_λ when $\hat{k}$ and E^* is given:

$$E_\lambda = E^* (A - \alpha_\lambda) \quad (A-10)$$

On the other hand, we may seek E_λ^* for given $\hat{k}$ and E . We eliminate $\tilde{\alpha}$ from (A-7) and obtain

$$\alpha^3 - 3e^2\alpha + c_0 + \frac{\Delta_0}{E} (A - \alpha) (\alpha^2 - e^2) = 0 \quad (A-11)$$

and from the solutions α_λ we find

$$E_\lambda^* = E (A - \alpha_\lambda)^{-1} \quad (A-12)$$

$$\tilde{\alpha}_\lambda = \frac{\Delta_0}{E} (A - \alpha_\lambda) \quad (A-13)$$

Equations (A-7) or (A-11) are solved by standard numerical techniques. Once α_λ and $\tilde{\alpha}_{(\lambda)}$ have been found, the calculation of the density-of-states and other quantities is rather straightforward.

For the density-of-states factor of a particular band λ (as used for example in (2-35)) we have

$$\tilde{D}_\lambda(\hat{k}, E) \equiv \left(\frac{E_\lambda^*}{E} \right)^{\frac{1}{2}} \frac{\partial E_\lambda^*}{\partial E} \quad (A-14)$$

$$= \beta_\lambda^{3/2} \left(1 + \frac{E}{A - \alpha_\lambda} \frac{\partial \alpha_\lambda}{\partial E} \right) \quad (A-15)$$

where we have used (A-1), (A-5) and (A-12). The derivative of α_λ is deduced from (A-11):

$$\left[3\alpha^2 - 3e^2 + 2\alpha\tilde{\alpha} - (\alpha^2 - e^2) \frac{\tilde{\alpha}}{A - \alpha} \right] \frac{\partial \alpha}{\partial E} = \frac{\tilde{\alpha}}{E} (\alpha^2 - e^2) \quad (A-16)$$

so that

$$\tilde{D}_\lambda(\hat{k}, E) = \beta_\lambda^{3/2} \left[1 - \frac{\alpha^2 - e^2}{3\alpha^2 - 3e^2 + 2\alpha\tilde{\alpha}} \cdot \frac{\tilde{\alpha}}{A - \alpha} \right]_\lambda^{-1} \quad (A-17)$$

For use later in connection with matrix elements, we need to know something about the eigenvectors of the matrix $\bar{\bar{H}}$, i.e., the quantities $F_{\lambda\mu j}$ appearing in (2-5) and (2-6). In particular, we seek an expression for the product

$$\tau_{jj'}(\lambda) = \sum_{\mu=1}^2 F_{\lambda\mu j} F_{\lambda\mu j'}^* \quad (A-18)$$

where j, j' counts the 6 basis states (2-9) and (2-10), λ the three bands, and $\mu = 1, 2$ the degenerate spin states in each band. The eigenvalue equation (2-5) with $\bar{\bar{H}}$ as in (2-12) is transformed into

$$\sum_{j'=1}^6 \{h'_{jj'} + \alpha \delta_{jj'}\} F_{j'} = 0 \quad (A-19)$$

where α was introduced in (A-5) and

$$\bar{\bar{h}}' = \bar{\bar{H}}/E^* - A\bar{\bar{I}} \quad (A-20)$$

or

$$\bar{\bar{h}}' = \left\{ \begin{array}{cccccc} b_s & h & j & 0 & h/\sqrt{2} & j\sqrt{2} \\ h^* & -b_s & 0 & j & -b_s\sqrt{2} & -h\sqrt{3}/2 \\ j^* & 0 & -b_s & -h & -h^*\sqrt{3}/2 & b_s\sqrt{2} \\ 0 & j^* & -h^* & b_s & -j^*\sqrt{2} & h^*/\sqrt{2} \\ h^*/\sqrt{2} & -b_s\sqrt{2} & -h\sqrt{3}/2 & -j\sqrt{2} & \tilde{\alpha} & 0 \\ j^*\sqrt{2} & -h^*\sqrt{3}/2 & b_s\sqrt{2} & h/\sqrt{2} & 0 & \tilde{\alpha} \end{array} \right\} \quad (A-21)$$

with

$$h = -d_2 + id_1$$

$$j = -b_a + id_3 \quad (A-22)$$

$$b_s = \frac{1}{2}B(\hat{k}_x^2 + \hat{k}_y^2 - 2\hat{k}_z^2), \quad b_a = \frac{\sqrt{3}}{2}B(\hat{k}_x^2 - \hat{k}_y^2) \quad (A-23)$$

$$d_1 = D\hat{k}_y\hat{k}_z, \quad d_2 = D\hat{k}_z\hat{k}_x, \quad d_3 = D\hat{k}_x\hat{k}_y$$

and $\tilde{\alpha}$ defined in (A-6).

The matrix $\bar{\tau}$ in (A-18) has the same eigenvectors $\bar{F}$ as $\bar{h}'$ since by orthonormality

$$\begin{aligned} \sum_{j'=1}^6 \tau_{jj'}(\lambda) F_{\lambda', \mu', j'} &= \sum_{j'=1}^6 \sum_{\mu=1}^2 F_{\lambda \mu j} F_{\lambda \mu j}^* F_{\lambda \mu j'} \\ &= \sum_{\mu=1}^2 F_{\lambda \mu j} \delta_{\lambda \lambda'} \delta_{\mu \mu'} \\ &= \delta_{\lambda \lambda'} F_{\lambda \mu' j} \end{aligned} \quad (A-24)$$

It follows that the eigenvalues are 1 if $\lambda' = \lambda$, and 0 if $\lambda' \neq \lambda$. Such a matrix can be expressed in terms of $\bar{h}'$, and the eigenvalues $-\alpha$:

$$\begin{aligned} \bar{\tau}(\lambda) &= \frac{(\bar{h}' + \alpha_{\lambda'} \bar{I})(\bar{h}' + \alpha_{\lambda''} \bar{I})}{(\alpha_{\lambda'} - \alpha_{\lambda''})(\alpha_{\lambda'} - \alpha_{\lambda''})} \\ &= \frac{\bar{h}'^2 + (\alpha_{\lambda'} + \alpha_{\lambda''})\bar{h}' + \alpha_{\lambda'}\alpha_{\lambda''}\bar{I}}{\alpha_{\lambda'}^2 - (\alpha_{\lambda'} + \alpha_{\lambda''})\alpha_{\lambda'} + \alpha_{\lambda'}\alpha_{\lambda''}} \end{aligned} \quad (A-25)$$

where $\lambda \neq \lambda' \neq \lambda'' \neq \lambda$. From the equation (A-7) for α , we have

$$\alpha_{\lambda'}\alpha_{\lambda''} = -c_0 + \tilde{\alpha} e^2 \quad (A-26)$$

$$\alpha_{\lambda} + \alpha_{\lambda'} + \alpha_{\lambda''} = -\tilde{\alpha} \quad (\text{A-27})$$

i.e.

$$\alpha_{\lambda'} + \alpha_{\lambda''} = -\tilde{\alpha} - \alpha_{\lambda} \quad (\text{A-28})$$

$$\begin{aligned} \alpha_{\lambda}, \alpha_{\lambda''} &= \alpha_{\lambda}^{-1} (-c_0 + \tilde{\alpha} e^2) \\ &= \alpha_{\lambda}^{-1} [\alpha_{\lambda}^3 - 3e^2 \alpha_{\lambda} + \tilde{\alpha} (\alpha_{\lambda}^2 - e^2) + \tilde{\alpha} e^2] \\ &= \alpha_{\lambda}^2 + \alpha_{\lambda} \tilde{\alpha} - 3e^2 \end{aligned} \quad (\text{A-29})$$

where c_0 was eliminated by using (A-7). (A-25) is then

$$\bar{\tau}(\lambda) = \left[3\alpha_{\lambda}^2 - 3e^2 + 2\alpha_{\lambda} \tilde{\alpha} \right]^{-1} \left[\bar{h}^2 - (\alpha + \tilde{\alpha}) \bar{h} + (\alpha^2 + \alpha \tilde{\alpha} - 3e^2) \bar{I} \right] \quad (\text{A-30})$$

The index λ is now dropped, since α refers to band λ only. As shown in the next section, the $\bar{\tau}$ matrix has only 9 distinct (complex) components, and we shall postpone the evaluation of the elements until this has been established.

A.2. General form of squared matrix elements

Any relevant interaction Hamiltonian H_{int} will depend on the one-electron coordinates $\vec{r}$ and some non-electronic coordinates ξ , and it has the Bloch form

$$H_{\text{int}}(\xi, \vec{r}) = \sum_{\vec{q}} \exp(i\vec{q} \cdot \vec{r}) H_1(\xi, \vec{q}, \vec{r}) \quad (\text{A-31})$$

The electronic matrix element of each $\vec{q}$ component in (A-31) is by reference to the eigenfunctions ψ in (2-6):

$$\begin{aligned} \langle \psi(\lambda', \mu', \vec{k}') | \exp(i\vec{q} \cdot \vec{r}) H_1(\xi, \vec{q}, \vec{r}) | \psi(\lambda \mu \vec{k}) \rangle \\ = \delta_{\vec{k}-\vec{k}', \vec{q}} \sum_{jj'} F_{\lambda', \mu', j'}^*(\vec{k}') S_{j, j'}(\xi, \vec{q}) F_{\lambda \mu j}(\vec{k}) \end{aligned} \quad (\text{A-32})$$

where

$$S_{j,j}(\xi, \bar{q}) = \langle j' | H_1(\xi, \bar{q}, \bar{r}) | j \rangle \quad (A-33)$$

are the matrix elements of the interaction between the $k = 0$ basis states.

In transition rates, self-energies, and second-order perturbation theory appearing in the main text, the matrix element (A-32) occurs as absolute squared, and as a consequence of the Kramers degeneracy of the electronic energy bands, the squared matrix element will be averaged over initial states with common $\lambda \bar{k}$ and summed over final states with common $\lambda' \bar{k}'$. It is thus relevant to consider the quantity

$$\begin{aligned} U(\lambda' \bar{k}', \lambda \bar{k}) &= \frac{1}{2} \sum_{\mu \mu'} \left| \sum_{jj'} F_{\lambda', \mu', j'}^*(\bar{k}') S_{j', j} F_{\lambda \mu j}(\bar{k}) \right|^2 \\ &= \frac{1}{2} \sum_{ii'jj'=1}^6 \tau_{i', j'}^*(\lambda' \bar{k}') S_{i', i} S_{j', j}^* \tau_{ij}(\lambda \bar{k}) \end{aligned} \quad (A-34)$$

where τ_{ij} is defined in (A-18). This product is rather cumbersome to work out explicitly, but symmetry arguments will take us some of the way. The final goal here is to express U in terms of real quantities with optimum use of symmetry and cyclic permutation properties.

Let us start by writing

$$U = \frac{1}{2} \sum_{i', j'} \tau_{i', j'}^*(\lambda' \bar{k}') \Omega_{i', j'} \quad (A-35)$$

where

$$\Omega_{i', j'} = \sum_{ij} S_{i', i} S_{j', j}^* \tau_{ij}(\lambda \bar{k}) \quad (A-36)$$

The time-reversal operator is defined so that it transforms a state $(\lambda 1 \bar{k})$ into the state with opposite spin $(\lambda 2 \bar{k})$ and vice versa. From the definition of $\bar{\tau}$ as a sum over spin-states, it is obvious that $\bar{\tau}$ commutes with time-reversal. It can then be shown that the most general form of $\bar{\tau}$ is

$$\tau = \begin{Bmatrix} \tau_{11} & \tau_{12} & \tau_{24} & 0 & \tau_{15} & -\tau_{54} \\ * & & & & & \\ \tau_{12} & \tau_{22} & 0 & \tau_{24} & \tau_{25} & \tau_{53} \\ * & & & & & \\ \tau_{24} & 0 & \tau_{22} & -\tau_{12} & \tau_{53} & -\tau_{25} \\ * & & & & & \\ 0 & \tau_{24} & -\tau_{12} & \tau_{11} & \tau_{54} & \tau_{15} \\ * & & & & & \\ \tau_{15} & \tau_{25} & \tau_{53} & \tau_{54} & \tau_{55} & 0 \\ * & & & & & \\ -\tau_{54} & \tau_{53} & -\tau_{25} & \tau_{15} & 0 & \tau_{55} \end{Bmatrix} \quad (A-37)$$

Actually, all the spin-independent 6x6 matrices considered in this work has this form, however in many cases with some simplifications. In particular, the Ω -matrix (A-36) has this form.

It follows that U in (A-35) consists of 9 terms:

$$U = \tau'_{11}\Omega_{11} + \tau'_{22}\Omega_{22} + \tau'_{55}\Omega_{55} + 2\text{Re}\{\tau'_{12}\Omega_{12} \\ + \tau'_{24}\Omega_{24} + \tau'_{15}\Omega_{15} + \tau'_{53}\Omega_{53} + \tau'_{54}\Omega_{54} + \tau'_{25}\Omega_{25}\} \quad (A-38)$$

where τ' is short for $\tau(\lambda'\bar{k}')$. Before further development we use (A-30) to write out the 9 τ_{ij} elements. We shall then find that τ_{25} is real (as the diagonal elements τ_{ii}) and that $\tau_{53} = -\sqrt{3}\tau_{15}$. The number of independent real components is then 12. In order to make use of xyz-permutations we organize the τ 's in a 14-component vector $\bar{\sigma}$ with the following elements σ_i :

$$\begin{aligned} \sigma_1 &= \frac{1}{2}(\tau_{11} + \tau_{22}) - \tau_{55} &= \tilde{a}\alpha M^{-1} \\ \sigma_2 &= \frac{1}{2\sqrt{3}}(\tau_{11} - \tau_{22}) + \frac{1}{\sqrt{6}}\tau_{25} - \text{Re}\{\tau_{24} + \frac{1}{\sqrt{2}}\tau_{54}\} &= -\tilde{a}b_1 M^{-1} \\ \sigma_3 &= \frac{1}{2\sqrt{3}}(\tau_{11} - \tau_{22}) + \frac{1}{\sqrt{6}}\tau_{25} + \text{Re}\{\tau_{24} + \frac{1}{\sqrt{2}}\tau_{54}\} &= -\tilde{a}b_2 M^{-1} \end{aligned}$$

$$\begin{aligned}
 \sigma_4 &= -\frac{1}{\sqrt{3}}(\tau_{11} - \tau_{22}) - \sqrt{\frac{2}{3}}\tau_{25} &= -\tilde{\alpha}b_3M^{-1} \\
 \sigma_5 &= \text{Im}\{\tau_{12} - \sqrt{2}\tau_{15}\} &= -\tilde{\alpha}d_1M^{-1} \\
 \sigma_6 &= -\text{Re}\{\tau_{12} - \sqrt{2}\tau_{15}\} &= -\tilde{\alpha}d_2M^{-1} \\
 \sigma_7 &= \text{Im}\{\tau_{24} + \frac{1}{\sqrt{2}}\tau_{54}\} &= -\tilde{\alpha}d_3M^{-1} \\
 \sigma_8 &= \tau_{55} &= (\alpha^2 - e^2)M^{-1} \\
 \sigma_9 &= -\frac{1}{\sqrt{6}}\tau_{25} + \text{Re}\{\frac{1}{\sqrt{2}}\tau_{54}\} &= -(\alpha b_1 + b_{12})M^{-1} \\
 \sigma_{10} &= -\frac{1}{\sqrt{6}}\tau_{25} - \text{Re}\{\frac{1}{\sqrt{2}}\tau_{54}\} &= -(\alpha b_2 + b_{22})M^{-1} \\
 \sigma_{11} &= \sqrt{\frac{2}{3}}\tau_{25} &= -(\alpha b_3 + b_{32})M^{-1} \\
 \sigma_{12} &= \text{Im}\{\sqrt{2}\tau_{15}\} &= -(\alpha d_1 + d_{12})M^{-1} \\
 \sigma_{13} &= -\text{Re}\{\sqrt{2}\tau_{15}\} &= -(\alpha d_2 + d_{22})M^{-1} \\
 \sigma_{14} &= -\text{Im}\{\frac{1}{\sqrt{2}}\tau_{54}\} &= -(\alpha d_3 + d_{32})M^{-1}
 \end{aligned}$$

(A-39)

with $\alpha = \alpha_\lambda$ and

$$M = 3\alpha^2 - 3e^2 + 2\alpha\tilde{\alpha} \quad (\text{A-40})$$

$$\begin{aligned}
 e^2 &= \frac{1}{2}(b_1^2 + b_2^2 + b_3^2) + d_1^2 + d_2^2 + d_3^2 \\
 b_1 &= \frac{1}{\sqrt{3}}b_s + b_a = \frac{1}{\sqrt{3}}B(2\hat{k}_x^2 - \hat{k}_y^2 - \hat{k}_z^2) \\
 d_1 &= D\hat{k}_y\hat{k}_z
 \end{aligned}$$

(A-41)

$$b_{12} = \frac{1}{\sqrt{3}}(-2b_1^2 + b_2^2 + b_3^2 + 2d_1^2 - d_2^2 - d_3^2)$$

$$d_{12} = \sqrt{3}(b_1d_1 - d_2d_3)$$

and similar quantities obtained by cyclic permutation (123 ~ xyz) of the first index. b and d terms reflect Γ_{12} and Γ'_{25} symmetry, respectively, and so the transformation properties are:

$$\begin{aligned}\sigma_1, \sigma_8 & : \Gamma_1 \\ \sigma_2, \sigma_3, \sigma_4, \sigma_9, \sigma_{10}, \sigma_{11} & : \Gamma_{12} \\ \sigma_5, \sigma_6, \sigma_7, \sigma_{12}, \sigma_{13}, \sigma_{14} & : \Gamma'_{25}\end{aligned}$$

Near the band edge in the parabolic region we have $\alpha_\lambda \rightarrow -e_\lambda$ and $\tilde{\alpha}$ becomes very large so that $\sigma_8, \dots, \sigma_{14} \rightarrow 0$. This explains the 2×7 organisation.

We now continue the contraction in the expression (A-38) for U:

$$U = \sum_{n=1}^{14} \sigma_n' \tilde{\Omega}_n \quad (\text{A-42})$$

and the 14 components $\tilde{\Omega}_n$ will be given by the formulas

$$\tilde{\Omega}_1 = \Omega_{11} + \Omega_{22}$$

$$\tilde{\Omega}_2 = \frac{1}{2\sqrt{3}}(\Omega_{11} - \Omega_{22}) - \text{Re}\{\Omega_{24}\}$$

$$\tilde{\Omega}_3 = \frac{1}{2\sqrt{3}}(\Omega_{11} - \Omega_{22}) + \text{Re}\{\Omega_{24}\}$$

$$\tilde{\Omega}_4 = -\frac{1}{\sqrt{3}}(\Omega_{11} - \Omega_{22})$$

$$\tilde{\Omega}_5 = 2\text{Im}\{\Omega_{12}\}$$

$$\tilde{\Omega}_6 = -2\text{Re}\{\Omega_{12}\}$$

$$\tilde{\Omega}_7 = 2\text{Im}\{\Omega_{24}\}$$

$$\tilde{\Omega}_8 = \Omega_{11} + \Omega_{22} + \Omega_{55}$$

$$\begin{aligned}
\tilde{\Omega}_9 &= \frac{1}{2\sqrt{3}}(\Omega_{11} - \Omega_{22}) - \sqrt{\frac{2}{3}}\text{Re}\{\Omega_{25}\} - \text{Re}\{\Omega_{24} - \sqrt{2}\Omega_{54}\} \\
\tilde{\Omega}_{10} &= \frac{1}{2\sqrt{3}}(\Omega_{11} - \Omega_{22}) - \sqrt{\frac{2}{3}}\text{Re}\{\Omega_{25}\} + \text{Re}\{\Omega_{24} - \sqrt{2}\Omega_{54}\} \\
\tilde{\Omega}_{11} &= -\frac{1}{\sqrt{3}}(\Omega_{11} - \Omega_{22}) + 2\sqrt{\frac{2}{3}}\text{Re}\{\Omega_{25}\} \\
\tilde{\Omega}_{12} &= 2\text{Im}\{\Omega_{12}\} + \frac{1}{\sqrt{2}}\Omega_{15} - \sqrt{\frac{3}{2}}\Omega_{53} \\
\tilde{\Omega}_{13} &= -2\text{Re}\{\Omega_{12}\} + \frac{1}{\sqrt{2}}\Omega_{15} - \sqrt{\frac{3}{2}}\Omega_{53} \\
\tilde{\Omega}_{14} &= 2\text{Im}\{\Omega_{24} - \sqrt{2}\Omega_{54}\}
\end{aligned} \tag{A-43}$$

Finally, we shall write

$$\tilde{\Omega}_m = \sum_{n=1}^{14} \tilde{S}_{nm} \sigma_m \tag{A-44}$$

so that

$$U = \sum_{nm} \sigma_n^* \tilde{S}_{nm} \sigma_m \tag{A-45}$$

In order to evaluate $\tilde{S}$, we proceed from (A-36) defining Ω , through (A-43) giving $\tilde{\Omega}$, to the separation (A-44). We shall only show the first step explicitly. From (A-36) and (A-37)

$$\Omega_{ij} = (S_{i1}S_{j1}^* + S_{i4}S_{j4}^*)\tau_{11} + \dots \tag{A-46}$$

We suppress the indices i and j and use that τ_{25} is real and $\tau_{53} = -\sqrt{3}\tau_{15}$:

$$\begin{aligned}
\Omega &= (S_1S_1^* + S_4S_4^*)\tau_{11} + (S_2S_2^* + S_3S_3^*)\tau_{22} \\
&+ (S_5S_5^* + S_6S_6^*)\tau_{55} \\
&+ (S_2S_5^* - S_6S_3^* + S_5S_2^* - S_3S_6^*)\tau_{25}
\end{aligned}$$

$$\begin{aligned}
 & + (s_1 s_5^* + s_6 s_4^* - \sqrt{3} s_5 s_3^* - \sqrt{3} s_2 s_6^*) \tau_{15} \\
 & + (s_5 s_1^* + s_4 s_6^* - \sqrt{3} s_3 s_5^* - \sqrt{3} s_6 s_2^*) \tau_{15}^* \\
 & + (s_1 s_2^* - s_3 s_4^*) \tau_{12} + (s_2 s_1^* - s_4 s_3^*) \tau_{12}^* \\
 & + (s_5 s_4^* - s_1 s_6^*) \tau_{54} + (s_4 s_5^* - s_6 s_1^*) \tau_{54}^* \\
 & + (s_2 s_4^* + s_1 s_3^*) \tau_{24} + (s_4 s_2^* + s_3 s_1^*) \tau_{24}^* \quad (A-47)
 \end{aligned}$$

The general matrix $\bar{S}$ has the extended Shockley form and will be specified by symmetry elements only:

$$\begin{aligned}
 \tilde{f} &= \tilde{a} + \tilde{b}_s, & \tilde{g} &= \tilde{a} - \tilde{b}_s \\
 \tilde{h} &= -\tilde{d}_2 + i\tilde{d}_1, & \tilde{j} &= -\tilde{b}_a + i\tilde{d}_3
 \end{aligned} \quad (A-48)$$

where $\tilde{a} \sim \Gamma_1$, $\tilde{b} \sim \Gamma_{12}$, and $\tilde{d} \sim \Gamma'_{25}$.

$$\bar{S} = \left\{ \begin{array}{cccccc}
 \tilde{f} & \tilde{h} & \tilde{j} & 0 & \tilde{h}/\sqrt{2} & \tilde{j}\sqrt{2} \\
 \tilde{h}^* & \tilde{g} & 0 & \tilde{j} & -\tilde{b}_s\sqrt{2} & -\tilde{h}\sqrt{3} \\
 \tilde{j}^* & 0 & \tilde{g} & -\tilde{h} & -\tilde{h}^*\sqrt{3} & \tilde{b}_s\sqrt{2} \\
 0 & \tilde{j}^* & -\tilde{h}^* & \tilde{f} & -\tilde{j}^*\sqrt{2} & \tilde{h}^*/\sqrt{2} \\
 \tilde{h}^*/\sqrt{2} & -\tilde{b}_s\sqrt{2} & -\tilde{h}\sqrt{3} & -\tilde{j}\sqrt{2} & \tilde{a} & 0 \\
 \tilde{j}^*\sqrt{2} & -\tilde{h}^*\sqrt{3} & \tilde{b}_s\sqrt{2} & \tilde{h}/\sqrt{2} & 0 & \tilde{a}
 \end{array} \right\} \quad (A-49)$$

In the following we drop the tilde on these and similar symbols which are formally alike to the band structure quantities (A-41). Additional conglomerates are

$$a_0 = a^2 - e^2$$

$$b_{13} = \frac{2}{\sqrt{3}}(ab_1 + b_{12}) \quad (A-50)$$

$$d_{13} = \frac{2}{\sqrt{3}}(ad_1 + d_{12})$$

The resulting $\tilde{S}$ -matrix is expressed in terms of the following three 7×7 symmetric matrices:

$$\tilde{T}(1) = \left\{ \begin{array}{ccccccc} 4a^2 & 2ab_1 & 2ab_2 & 2ab_3 & 4ad_1 & 4ad_2 & 4ad_3 \\ & b_1^2 & b_1b_2 & b_1b_3 & 2b_1d_1 & 2b_1d_2 & 2b_1d_3 \\ & & b_2^2 & b_2b_3 & 2b_2d_1 & 2b_2d_2 & 2b_2d_3 \\ & & & b_3^2 & 2b_3d_1 & 2b_3d_2 & 2b_3d_3 \\ & & & & 4d_1^2 & 4d_1d_2 & 4d_1d_3 \\ & & & & & 4d_2^2 & 4d_2d_3 \\ & & & & & & 4d_3^2 \end{array} \right\} \quad (A-51)$$

$$\tilde{T}(2) = \left\{ \begin{array}{ccccccc} -6a_0 & 0 & 0 & 0 & 0 & 0 & 0 \\ & 2a_0 & -a_0 & -a_0 & 0 & 0 & 0 \\ & & 2a_0 & -a_0 & 0 & 0 & 0 \\ & & & 2a_0 & 0 & 0 & 0 \\ & & & & 6a_0 & 0 & 0 \\ & & & & & 6a_0 & 0 \\ & & & & & & 6a_0 \end{array} \right\} \quad (A-52)$$

$$\bar{T}^{(3)} = \begin{Bmatrix} -a_0 & -\frac{\sqrt{3}}{2}b_{13} & -\frac{\sqrt{3}}{2}b_{23} & -\frac{\sqrt{3}}{2}b_{33} & -\sqrt{3}d_{13} & -\sqrt{3}d_{23} & -\sqrt{3}d_{33} \\ & b_{13} & b_{33} & b_{23} & -2d_{13} & d_{23} & d_{33} \\ & & b_{23} & b_{13} & d_{13} & -2d_{23} & d_{33} \\ & & & b_{33} & d_{13} & d_{23} & -2d_{33} \\ & & & & -3b_{13} & 3d_{33} & 3d_{23} \\ & & & & & -3b_{23} & 3d_{13} \\ & & & & & & -3b_{33} \end{Bmatrix}$$

(A-53)

Then for $i, j = 1, \dots, 7$ we have

$$\begin{aligned} \tilde{S}_{ij} &= T_{ij}^{(1)} + \frac{1}{3}T_{ij}^{(2)} \\ \tilde{S}_{i,7+j} &= 3(1-\frac{1}{2}\delta_{j1})T_{ij}^{(1)} + \frac{1}{3}T_{ij}^{(2)} + (1+\delta_{i1})T_{ij}^{(3)} \\ \tilde{S}_{7+i,j} &= \tilde{S}_{j,7+i} \\ \tilde{S}_{7+i,7+j} &= 3a_0\delta_{i1}\delta_{j1} + 9(1-\frac{1}{2}\delta_{j1})(1-\frac{1}{2}\delta_{i1})T_{ij}^{(1)} \\ &\quad + T_{ij}^{(2)} + 3T_{ij}^{(3)} \end{aligned} \quad (A-54)$$

In Appendix B, considerable simplifications are achieved for the interactions studied in the present work. However, the general result for the squared matrix element U may have many applications elsewhere, e.g. transport properties, dielectric function, and polaron dispersion.

Appendix B: Hole-phonon interaction

B.1. Adiabatic approximation

Without going into much detail we shall sketch the application of the adiabatic approximation to semiconductors in order to elucidate the nature of the electron-phonon interaction and the direct dependence of the phonon system on the state of the electronic system.

The crystal Hamiltonian is

$$H = T_e + V_{ee} + V_{ei} + T_i + V_{ii} \quad (B-1)$$

where T_e and T_i are the kinetic energy of the electrons and the ions, and V_{ee} , V_{ii} , and V_{ei} are the interaction potentials of electrons, ions, and electrons and ions, respectively. The Schrödinger equation for the crystal is

$$H\Psi(r_i, R_j) = E\Psi(r_i, R_j) \quad (B-2)$$

with r_i and R_j being the electronic, respectively the ionic coordinates.

The adiabatic approximation consists in considering T_i as a small perturbation, but this leaves many versions of adiabatic approximations, from which we choose the so-called static approximation. Thus we solve the electronic problem for ions fixed in their equilibrium lattice positions (the only realistic possibility), but since this equilibrium will actually depend on the solution, the approach is not entirely consistent.

$$\left[T_e + V_{ee} + V_{ei}^O + V_{ii}^O \right] \phi_n^O(r_i) = E_n^O \phi_n^O(r_i) \quad (B-3)$$

where E_n^O and ϕ_n^O describe the electronic state. We now expand Ψ in the system ϕ_n^O

$$\Psi(r_i, R_j) = \sum_n \chi_n(R_j) \phi_n^O(r_i) \quad (B-4)$$

and obtain by insertion in (B-2) the following equation

$$\left[T_i + (V_{ii} - V_{ii}^O) + W_{nn} + E_n^O - E \right] \chi_n + \sum_{n' \neq n} W_{nn'} \chi_{n'} = 0 \quad (B-5)$$

where

$$W_{nn'} = \int d^3 r_i \phi_n^{O*} (V_{ei} - V_{ei}^O) \phi_{n'}^O \quad (B-6)$$

Neglecting the last term in eq. (B-5) we get the eigenvalue equation for the lattice vibrations. The neglected term is the off-diagonal elements of the electron-phonon interaction Hamiltonian

$$H_{int} = V_{ei} - V_{ei}^O \quad (B-7)$$

Note that the diagonal element W_{nn} is included in the lattice Hamiltonian in (B-5), and so the equilibrium ion positions depend on the electronic state. In the present work it is important to observe that W_{nn} also gives a direct dependence of phonon energies on the electronic state. We shall call it the direct second-order contribution since it originates in the second-order expansion of W in the ionic displacements u_j from equilibrium.

The interaction (B-7) forms the basis of deformation potential theory. In the one-electron model for the electronic system, $(V_{ei} - V_{ei}^O)$ is replaced by the self-consistent one-electron potential and is expanded to first order in ionic displacements $\bar{u}_{jt}$ from equilibrium $\bar{R}_{jt}$

$$H_{int} = \sum_{jt} \bar{u}_{jt} \cdot \bar{V}_{jt} \quad (B-8)$$

with j indicating the unit cell and t the particular ion in the cell. The displacements are given by the normal mode expansion

$$\bar{u}_{jt} = i \sum_{qs} \left(\frac{\hbar}{2\rho V \omega_{qs}} \right)^{\frac{1}{2}} \frac{m_1 + m_2}{2\sqrt{m_1 m_2}} \left[a_{qs}^- \exp(i\bar{q} \cdot \bar{R}_{jt}) \bar{e}_{qst}^- - a_{qs}^+ \exp(-i\bar{q} \cdot \bar{R}_{jt}) \bar{e}_{qst}^{*+} \right] \quad (B-9)$$

where ρ is the mass density, V the crystal volume, and m_t the masses of the ions in the cell. ω_{qs}^- and $\bar{e}_{qst}^-$ are frequency and polarisation vectors of the mode with wave vector $\bar{q}$ in branch s , and a_{qs}^- and a_{qs}^+ are annihilation and creation operators. The polarisation vectors $\bar{e}$ are unit vectors.

For long-wavelength optic phonons ($\bar{q} \rightarrow 0$) the two sublattices of the diamond (and zincblende) structure vibrate in opposite phase, i.e.,

$$\bar{e}_2 = -\bar{e}_1 \equiv -\bar{e}_0 \quad (B-10)$$

and so for this case (B-8) can be written in the form (A-31)

$$H_{int} = \sum_{\bar{q}} \exp(i\bar{q} \cdot \bar{r}) \sum_s \frac{1}{2} u_{os} \bar{e}_{os} \cdot \bar{U}_{os}(\bar{q}, \bar{r}) \quad (B-11)$$

where the strain amplitude is

$$\frac{1}{2} u_{os} = \left(\frac{\hbar}{2\rho V \omega_{os} a_c^2} \right)^{\frac{1}{2}} \frac{m_1 + m_2}{2\sqrt{m_1 m_2}} i (a_{os} - a_{os}^+) \quad (B-12)$$

a_c is the cube-edge lattice constant, and

$$\bar{U}_{os}(\bar{q}, \bar{r}) = a_c \sum_{jt} (-1)^{t+1} \bar{v}_{jt} \exp[i\bar{q} \cdot (\bar{R}_{jt} - \bar{r})] \quad (B-13)$$

The matrix element of (B-12) between two states of the phonon system differing by one phonon is

$$A_{os} = \left(\frac{\hbar}{2\rho V \omega_{os} a_c^2} \right)^{\frac{1}{2}} \frac{m_1 + m_2}{2\sqrt{m_1 m_2}} \left[n_{os} + \frac{1}{2} \pm \frac{1}{2} \right]^{\frac{1}{2}} \quad (B-14)$$

where n_{os} is the initial number of phonons in the mode ($\bar{q}s$) and the $\pm$ sign refers to emission, respectively absorption of one phonon. In the following the dependence on s will be neglected.

Since $\frac{1}{2}u_o\bar{e}_o$ is related to the internal strain in the unit cell, $\bar{u}_o$ is obviously some sort of deformation potential. The behavior of $\bar{u}_o$ for $q \rightarrow 0$ suggests a distinction (Lawaetz 1969) between the actual deformation potential and multipole contributions, the latter again divided into a nonpolar quadrupole part and a polar dipole part. Whereas the nonpolar interactions are always present, the polar part occurs only in polar materials. The multipole elements arise from the non-analytic behavior of the lattice sum in (B-13) for $q \rightarrow 0$ if $\bar{v}_{jt}$ contains long-range potentials of Coulomb character. For more detail the reader is referred to the literature (Lawaetz 1969, Vogl 1976). Here we only give the result for the matrix elements $S_{j,j}$ in (A-33), (A-48), and (A-49).

For the nonpolar interaction we find

$$\begin{aligned}\tilde{a}_n &= A_o a_1 \left[e_{osx} \hat{q}_y \hat{q}_z + e_{osy} \hat{q}_z \hat{q}_x + e_{osz} \hat{q}_x \hat{q}_y \right] \\ \tilde{b}_{ni} &= 0 \\ \tilde{d}_{ni} &= A_o d_o e_{osi} \quad (i = 1, 2, 3)\end{aligned}\tag{B-15}$$

where d_o is the optic deformation potential (-constant) and a_1 is a quadrupole parameter ($a_1 = C_o a_c$ for C_o as defined by the author (Lawaetz 1969)).

For polar materials we have in addition to (B-15)

$$\tilde{a}_p = iA_o \frac{2e_o e_c^* a_c}{\Omega q^2} \bar{e}_{os} \cdot \bar{q}\tag{B-16}$$

where the Callen charge is given by

$$(e_c^*)^2 = \frac{m_1 m_2}{m_1 + m_2} \Omega \omega_L^2 (\epsilon_\infty^{-1} - \epsilon_s^{-1})\tag{B-17}$$

e_o is the elementary charge, Ω is the volume of the unit cell

$$\Omega = \frac{1}{4} a_c^3\tag{B-18}$$

L means longitudinal optic, and ϵ_s and ϵ_∞ are the static and high-frequency dielectric constants. The imaginary "i" in (B-16) indicates that the nonpolar and polar potentials are out of phase, and so the squared matrix elements should be added after separate treatments of each interaction.

B.2. Particular squared matrix elements

In this section we combine the results of sections A.2 and B.1 to give the squared matrix elements relevant for the problems in the present work: (a) hole scattering $(\lambda, \bar{k}) \rightarrow (\lambda', \bar{k} + \bar{q})$ for vanishing $\bar{q}$ (phonon self-energy), and (b) hole scattering $(\lambda, 0) \rightarrow (\lambda', \bar{k} = \bar{q})$ (hole self-energy).

In the first case we are interested in the squared matrix element for the absorption of one optic phonon with $\bar{q} \rightarrow 0$ in elemental semiconductors ($m_1 = m_2$). Due to the triple degeneracy we can average over 3 arbitrary perpendicular polarisation directions. The result is written in the form

$$\left| H_{\lambda\lambda}^O(\bar{k}) \right|^2 = \frac{\hbar d_O^2}{2\rho\omega a_c^2} g_{\lambda\lambda}(\bar{k}) \quad (\text{B-19})$$

Here we have assumed unit volume V. For the calculation of the phonon self-energy only $\lambda \neq \lambda'$ is relevant, and it is easily shown that the multipole contribution to these inter-band matrix elements vanishes. However, for the analogous calculation of the change in elastic constant C_{44} we shall need also the $\lambda = \lambda'$ form of (B-19), and here the multipole term is absent. From (B-14) and (B-15) we find

$$g_{\lambda\lambda} = \sum_{i,j=1}^{14} \sigma_{\lambda,i} \left[\frac{1}{3} \sum_s \tilde{S}_{ij} (\tilde{d}_1 = e_{os1} \text{ etc.}) \right] \sigma_{\lambda,j} \quad (\text{B-20})$$

The summation over s in the matrices (A-51)-(A-53) is performed by setting

$$\begin{aligned} \tilde{d}_1^2 &= \tilde{d}_2^2 = \tilde{d}_3^2 = 1 \\ \tilde{a}_0 &= -\tilde{e}^2 = -3 \end{aligned} \quad (\text{B-21})$$

and all other combinations to zero. The result is

$$\begin{aligned}
 g_{\lambda\lambda} = & 2\sigma_1'\sigma_1 + 4(\sigma_1'\sigma_8 + \sigma_8'\sigma_1) + 6\sigma_8'\sigma_8 \\
 & - \frac{2}{3}(\sigma_2'\sigma_2 + \sigma_3'\sigma_3 + \sigma_4'\sigma_4) \\
 & - \frac{2}{3}(\sigma_2'\sigma_9 + \sigma_3'\sigma_{10} + \sigma_4'\sigma_{11} + \sigma_9'\sigma_2 + \sigma_{10}'\sigma_3 + \sigma_{11}'\sigma_4) \\
 & - 2(\sigma_9'\sigma_9 + \sigma_{10}'\sigma_{10} + \sigma_{11}'\sigma_{11}) \\
 & + \frac{1}{3}(\sigma_2'\sigma_3 + \sigma_3'\sigma_4 + \sigma_4'\sigma_2 + \sigma_3'\sigma_2 + \sigma_4'\sigma_3 + \sigma_2'\sigma_4) \\
 & + \frac{1}{3}(\sigma_2'\sigma_{10} + \sigma_3'\sigma_{11} + \sigma_4'\sigma_9 + \sigma_{10}'\sigma_2 + \sigma_{11}'\sigma_3 + \sigma_9'\sigma_4 \\
 & \quad + \sigma_2'\sigma_{11} + \sigma_3'\sigma_9 + \sigma_4'\sigma_{10} + \sigma_{11}'\sigma_2 + \sigma_9'\sigma_3 + \sigma_{10}'\sigma_4) \\
 & + (\sigma_9'\sigma_{10} + \sigma_{10}'\sigma_{11} + \sigma_{11}'\sigma_9 + \sigma_{10}'\sigma_9 + \sigma_{11}'\sigma_{10} + \sigma_9'\sigma_{11}) \\
 & - \frac{2}{3}(\sigma_5'\sigma_5 + \sigma_6'\sigma_6 + \sigma_7'\sigma_7) \\
 & + 2(\sigma_5'\sigma_{12} + \sigma_6'\sigma_{13} + \sigma_7'\sigma_{14} + \sigma_{12}'\sigma_5 + \sigma_{13}'\sigma_6 + \sigma_{14}'\sigma_7) \\
 & + 6(\sigma_{12}'\sigma_{12} + \sigma_{13}'\sigma_{13} + \sigma_{14}'\sigma_{14})
 \end{aligned}
 \tag{B-22}$$

For the present case $\bar{k}$ is the same in σ and σ' , and further simplification is straightforward. Introducing the explicit expressions from (A-39) and (A-40), we obtain the following.

$$\begin{aligned}
 M_{\lambda} M_{\lambda} g_{\lambda\lambda} = & 2\tilde{\alpha}^2 \alpha' \alpha + 4\tilde{\alpha} \left[\alpha' (\alpha^2 - e^2) + \alpha (\alpha'^2 - e^2) \right] + \\
 & + 6(\alpha^2 - e^2) (\alpha'^2 - e^2) - \tilde{\alpha}^2 (b_1^2 + b_2^2 + b_3^2) \\
 & - \tilde{\alpha} \left[(\alpha + \alpha') (b_1^2 b_2^2 + b_3^2) + 2(b_1 b_{12} + b_2 b_{22} + b_3 b_{32}) \right]
 \end{aligned}$$

$$\begin{aligned}
 & -3 \left[\alpha \alpha' (b_1^2 + b_2^2 + b_3^2) + (\alpha + \alpha') (b_1 b_{12} + b_2 b_{22} + b_3 b_{32}) \right. \\
 & \quad \left. + (b_{12}^2 + b_{22}^2 + b_{32}^2) \right] \\
 & - \frac{2}{3} \tilde{\alpha}^2 (d_1^2 + d_2^2 + d_3^2) \\
 & + 2 \tilde{\alpha} \left[(\alpha + \alpha') (d_1^2 + d_2^2 + d_3^2) + 2 (d_1 d_{12} + d_2 d_{22} + d_3 d_{32}) \right] \\
 & + 6 \left[\alpha \alpha' (d_1^2 + d_2^2 + d_3^2) + (\alpha + \alpha') (d_1 d_{12} + d_2 d_{22} + d_3 d_{32}) \right. \\
 & \quad \left. + (d_{12}^2 + d_{22}^2 + d_{32}^2) \right] \tag{B-23}
 \end{aligned}$$

where $\alpha' = \alpha_\lambda$, and $\alpha = \alpha_\lambda$. Here we insert

$$\begin{aligned}
 e^2 &= B^2 (1 - 3\mu_4) + D^2 \mu_4 \\
 e^4 &= B^4 (1 - 6\mu_4 + 9\mu_4^2) + B^2 D^2 (2\mu_4 - 6\mu_4^2) + D^4 \mu_4^2 \\
 b_1^2 + b_2^2 + b_3^2 &= 2B^2 (1 - 3\mu_4) \\
 b_1 b_{12} + b_2 b_{22} + b_3 b_{32} &= -B^3 (2 - 9\mu_4 + 27\mu_6) - BD^2 (\mu_4 - 9\mu_6) \\
 b_{12}^2 + b_{22}^2 + b_{32}^2 &= 2B^4 (1 - 6\mu_4 + 9\mu_4^2) + 2B^2 D^2 (\mu_4 + 9\mu_6 - 6\mu_4^2) \\
 &\quad + 2D^4 (-3\mu_6 + \mu_4^2) \\
 d_1^2 + d_2^2 + d_3^2 &= D^2 \mu_4 \\
 d_1 d_{12} + d_2 d_{22} + d_3 d_{32} &= -BD^2 (\mu_4 - 9\mu_6) - 3\sqrt{3} D^3 \mu_6 \\
 d_{12}^2 + d_{22}^2 + d_{32}^2 &= B^2 D^2 (\mu_4 - 9\mu_6) + 3D^4 \mu_6 \tag{B-24}
 \end{aligned}$$

The final result is

$$\begin{aligned}
 M_{\lambda} M_{\lambda}, g_{\lambda\lambda}, &= 2\tilde{\alpha}^2 (\alpha\alpha' - \gamma_1 - \frac{1}{3}\gamma_2) \\
 &+ 2\tilde{\alpha}(\alpha + \alpha') (2\alpha\alpha' - 3\gamma_1 - \gamma_2) \\
 &- 6(\alpha + \alpha')^2 (\gamma_1 + \gamma_2) \\
 &+ 6\alpha\alpha' (\alpha\alpha' + \gamma_1 + 3\gamma_2) \\
 &+ (3\alpha + 3\alpha' + 2\tilde{\alpha})\gamma_3 + \gamma_4
 \end{aligned} \tag{B-25}$$

$$\begin{aligned}
 \gamma_1 &= B^2(1-3\mu_4), \quad \gamma_2 = D^2\mu_4 \\
 \gamma_3 &= B^3(2-9\mu_4+27\mu_6) - BD^2(\mu_4-9\mu_6) - 6\sqrt{3}D^3\mu_6 \\
 \gamma_4 &= 12B^2D^2(\mu_4 - 9\mu_6) + 36D^4\mu_6 \\
 M_{\lambda} &= 3\alpha^2 - 3e^2 + 2\alpha\tilde{\alpha}
 \end{aligned} \tag{B-26}$$

As an illustration, we shall find $g_{\lambda\lambda}$, in the parabolic region where $\alpha_1 \rightarrow e$, $\alpha_2 \rightarrow -e$, and $\alpha_3 \rightarrow -\tilde{\alpha} \rightarrow -\infty$. (B-25) and (B-26) give in this limit

$$\begin{aligned}
 g_{11} &= g_{22} = \frac{\gamma_2}{3(\gamma_1 + \gamma_2)} \\
 g_{12} &= 1 - g_{11} \\
 g_{13} &= g_{23} = 1 \\
 g_{33} &= 0
 \end{aligned} \tag{B-27}$$

The first two lines are in accord with the parabolic results obtained in Chapters 3 and 4 by entirely different (and more simple) methods.

In the second case with scattering from $(\lambda, 0)$ to $(\lambda', \bar{k}=\bar{q})$, we treat the nonpolar and polar contributions independently.

Since compound semiconductors are involved, we retain the reduced-mass factor in A_0 (B-14), but we take the average over the three polarisation directions. For the nonpolar part we have (again for the absorption of one phonon averaged over polarisation directions)

$$\left| H_{\lambda\lambda}^{\text{no}}, (0, \vec{k}) \right|^2 = \frac{\hbar}{2\rho\omega a_c^2} \frac{(m_1 + m_2)^2}{4m_1 m_2} \times (d_o^2 g_{\lambda\lambda}^{n1} + d_o a_1 g_{\lambda\lambda}^{n2} + a_1^2 g_{\lambda\lambda}^{n3}) \quad (\text{B-28})$$

The coefficient $g_{\lambda\lambda}^{n1}$, of d_o^2 is obtained from (B-22) by taking σ_i in the parabolic limit for small $\vec{k}$:

$$\begin{aligned} \lambda = 1, 2: \quad \sigma_1 &= \frac{\tilde{\alpha}\alpha}{3\alpha^2 - 3e^2 + 2\alpha\tilde{\alpha}} \rightarrow \frac{1}{2} \\ \sigma_2 &\rightarrow b_1/2e_\lambda, \quad \sigma_3 \rightarrow b_2/2e_\lambda, \quad \sigma_4 \rightarrow b_3/2e_\lambda \\ \sigma_5 &\rightarrow d_1/2e_\lambda, \quad \sigma_6 \rightarrow d_2/2e_\lambda, \quad \sigma_7 \rightarrow d_3/2e_\lambda \\ \sigma_8, \dots, \sigma_{14} &\rightarrow 0 \end{aligned} \quad (\text{B-29})$$

These two bands are degenerate at $k = 0$ so that the average σ_i is relevant. We shall indicate this procedure by the index $\lambda = 0$:

$$\underline{\lambda = 0} : \quad \sigma_1 = \frac{1}{2} ; \quad \sigma_2, \dots, \sigma_{14} = 0 \quad (\text{B-30})$$

Further for $\lambda = 3$, $\alpha_3 \rightarrow A - \tilde{\alpha} \rightarrow -\infty$:

$$\begin{aligned} \underline{\lambda = 3} : \quad \sigma_1 &= -1 ; \quad \sigma_2, \dots, \sigma_7 = 0 \\ \sigma_8 &= 1 ; \quad \sigma_9, \dots, \sigma_{14} = 0 \end{aligned} \quad (\text{B-31})$$

Using (B-22) we then obtain

$$g_{0\lambda}^{n1} = \sigma_1' + 2\sigma_8' = \frac{2\alpha'^2 - 2e^2 + \tilde{\alpha}\alpha'}{3\alpha'^2 - 3e^2 + 2\tilde{\alpha}\alpha'} \quad (B-32)$$

$$g_{3\lambda}^{n1} = 2\sigma_1' + 2\sigma_8' = \frac{2\alpha'^2 - 2e^2 + 2\tilde{\alpha}\alpha'}{3\alpha'^2 - 3e^2 + 2\tilde{\alpha}\alpha'}$$

Following (B-15), the nonpolar quadrupole interaction contributes only to terms of type $\tilde{a}$. Thus the coefficient $g_{\lambda\lambda}^{n3}$, of a_1^2 in (B-28) is deduced by taking

$$\begin{aligned} \frac{1}{3} \sum_s \tilde{a}_s^2 &= \frac{1}{3} a_1^2 \sum_s (e_{osx} \hat{q}_y \hat{q}_z + e_{osy} \hat{q}_z \hat{q}_x + e_{osz} \hat{q}_x \hat{q}_y)^2 \\ &= \frac{1}{3} a_1^2 (\hat{q}_y^2 \hat{q}_z^2 + \hat{q}_z^2 \hat{q}_x^2 + \hat{q}_x^2 \hat{q}_y^2) \\ &= \frac{1}{3} a_1^2 \mu_4(\hat{k}) \end{aligned} \quad (B-33)$$

because $\vec{q} = \vec{k}$. Eqs. (B-30) and (B-31) show that only the first and eighth columns in the S-matrix are needed. The result including (B-33) is the only nonzero elements

$$\tilde{S}_{11} = \tilde{S}_{18} = \tilde{S}_{81} = \frac{2}{3} a_1^2 \mu_4; \quad \tilde{S}_{88} = a_1^2 \mu_4 \quad (B-34)$$

In combination with (B-30) and (B-31) this yields

$$g_{0\lambda}^{n3} = \frac{1}{3} (\sigma_1' + \sigma_8') \mu_4 = \frac{1}{3} \mu_4 \frac{\alpha'^2 - e^2 + \tilde{\alpha}\alpha'}{3\alpha'^2 - 3e^2 + 2\tilde{\alpha}\alpha'}$$

$$g_{3\lambda}^{n3} = \frac{1}{3} \sigma_8' \mu_4 = \frac{1}{3} \mu_4 \frac{\alpha'^2 - e^2}{3\alpha'^2 - 3e^2 + 2\tilde{\alpha}\alpha'} \quad (B-35)$$

The coefficient $g_{\lambda\lambda}^{n2}$, of a_1^2 in (B-28) is found by consideration of the terms with ad_1 , ad_2 , and ad_3 :

$$\begin{aligned}
 \frac{1}{3} \sum_s \tilde{a} d_1 &= \frac{1}{3} a_1 d_0 \sum_s (e_{osx} \hat{c}_y \hat{c}_z + e_{osy} \hat{c}_z \hat{c}_x + e_{osz} \hat{c}_x \hat{c}_y) e_{osx} \\
 &= \frac{1}{3} a_1 d_0 \hat{c}_y \hat{c}_z \\
 &= \frac{1}{3} a_1 d_0 \hat{k}_y \hat{k}_z \\
 &= \frac{a_1 d_0}{3D} d_1(\hat{k})
 \end{aligned} \tag{B-36}$$

The first and eighth columns of the $\tilde{S}$ -matrix for these terms are

$$\begin{aligned}
 \tilde{S}_{11} &= \begin{pmatrix} 0 & 0 & 0 & 0 & 4\tilde{a}d_1 & 4\tilde{a}d_2 & 4\tilde{a}d_3 \\ & 0 & 0 & 0 & 8\tilde{a}d_1 & 8\tilde{a}d_2 & 8\tilde{a}d_3 \end{pmatrix} \\
 \tilde{S}_{i8} &= \begin{pmatrix} 0 & 0 & 0 & 0 & 4\tilde{a}d_1 & 4\tilde{a}d_2 & 4\tilde{a}d_3 \\ & 0 & 0 & 0 & 12\tilde{a}d_1 & 12\tilde{a}d_2 & 12\tilde{a}d_3 \end{pmatrix}
 \end{aligned} \tag{B-37}$$

or with (B-36)

$$\begin{aligned}
 \tilde{S}_{11} &= \frac{4a_1 d_0}{3D} \{0 \ 0 \ 0 \ 0 \ d_1 \ d_2 d_3 \ 0 \ 0 \ 0 \ 0 \ 2d_1 \ 2d_2 \ 2d_3\} \\
 \tilde{S}_{i8} &= \frac{4a_1 d_0}{3D} \{0 \ 0 \ 0 \ 0 \ d_1 \ d_2 \ d_3 \ 0 \ 0 \ 0 \ 0 \ 3d_1 \ 3d_2 \ 3d_3\}
 \end{aligned} \tag{B-38}$$

The final result is obtained by using (B-30), (B-31), (A-39) and (B-24):

$$\begin{aligned}
 \eta_{o\lambda}^{n2} &= \frac{2}{3D} \left[d_1(\sigma_5' + 2\sigma_{12}') + d_2(\sigma_6' + 2\sigma_{13}') + d_3(\sigma_7' + 2\sigma_{14}') \right] \\
 &= \frac{2}{3D} \frac{(\tilde{\alpha} + 2\alpha') (d_1^2 + d_2^2 + d_3^2) + 2(d_1 d_{12} + d_2 d_{22} + d_3 d_{32})}{3\alpha'^2 - 3e^2 + 2\tilde{\alpha}\alpha'} \\
 &= \frac{4}{3D} \frac{-(\frac{1}{2}\alpha + \alpha')\gamma_2 + \gamma_5}{3\alpha'^2 - 3e^2 + 2\tilde{\alpha}\alpha'}
 \end{aligned} \tag{B-39a}$$

$$g_{3\lambda}^{n2} = \frac{4}{3D} \left[d_1 \sigma'_{12} + d_2 \sigma'_{13} + d_3 \sigma'_{14} \right]$$

$$= \frac{4}{3D} \frac{-\alpha' \gamma_2 + \gamma_5}{3\alpha'^2 - 3e^2 + 2\tilde{\alpha}\alpha'} \quad (B-39b)$$

with

$$\gamma_5 = BD^2(\mu_4 - 9\mu_6) + 3\sqrt{3}D^3\mu_6 \quad (B-40)$$

Finally, the polar scattering term expressed in the form (B-28) is written as

$$|H_{\lambda\lambda}^{po}, (0, \vec{k})|^2 = \frac{\hbar}{2\rho\omega a_c^2} \frac{(m_1 + m_2)^2}{4m_1 m_2} a_p^2 g_{\lambda\lambda}^p \quad (B-41)$$

with

$$a_p^2 = \frac{8e_o^2}{a_c} (\epsilon_\infty^{-1} - \epsilon_s^{-1}) \frac{m_1 m_2}{m_1 + m_2} \frac{(\hbar\omega)^2}{m\Delta_o} \quad (B-42)$$

and $g_{\lambda\lambda}^p$ is found from (B-16) by taking

$$\frac{1}{3} \sum_s \tilde{a}_s^2 = \frac{1}{3} a_p^2 \tilde{\alpha} \sum_s (\vec{e}_{os} \cdot \hat{k})^2$$

$$= \frac{1}{3} a_p^2 \tilde{\alpha} \quad (B-43)$$

so that by analogy with (B-33) we obtain

$$g_{o\lambda}^p = \frac{1}{3} \tilde{\alpha} (\sigma'_1 + \sigma'_8) = \frac{1}{3} \tilde{\alpha} \frac{\alpha'^2 - e^2 + \tilde{\alpha}\alpha'}{3\alpha'^2 - 3e^2 + 2\tilde{\alpha}\alpha'} \quad (B-44)$$

$$g_{3\lambda}^p = \frac{1}{3} \tilde{\alpha} \sigma'_8 = \frac{1}{3} \tilde{\alpha} \frac{\alpha'^2 - e^2}{3\alpha'^2 - 3e^2 + 2\tilde{\alpha}\alpha'}$$

Note that the polar interaction, which occurs for longitudinal optic phonons only, has also been averaged over the three polarisation directions in order to fit the form (B-28). The total averaged squared matrix element for the absorption of one optic phonon with arbitrary polarisation is thus (for unit volume)

$$|H_{\lambda\lambda}, (0, \vec{k})|^2 = \frac{\hbar}{2\rho\omega a_c} (d_{O\lambda\lambda}^2 g_{\lambda\lambda}^{n1} + a_1 d_{O\lambda\lambda}^2 g_{\lambda\lambda}^{n2} + a_1^2 g_{\lambda\lambda}^{n3} + a_p^2 g_{\lambda\lambda}^p) \frac{(m_1 + m_2)^2}{4m_1 m_2} \quad (B-45)$$

with g-coefficients given in (B-32), (B-39), (B-35), and (B-44).

B.3. Screening by free carriers

The dominant part of this work deals with virtual and real phonon scattering for large concentrations of free holes. The screening effect of these carriers may therefore be very important in several respects: changes in band structure, influence on impurity levels, and screening of the hole-phonon interaction. Here we shall be concerned only with the last feature which would have the most direct effect on our results. However, the following discussion concludes that the optic deformation potential, in the way it appears in the phonon renormalization, remains unaffected by the carriers, and this is why the problem is referred to an appendix. Furthermore, the present arguments will be limited to the problem at hand, and no complete screening theory exists for charged particles in the complex valence-band structure.

The subsequent treatment is a slight generalisation of the method used for a simple band structure (Boguslawski and Mycielski 1977). Let us start by writing down the Fourier expansion of the $\vec{q}$ component of the interaction potential (B-11):

$$H_{int}(\vec{q}) = \sum_{\vec{G}} \exp[i(\vec{q} + \vec{G}) \cdot \vec{r}] \phi(\vec{q}, \vec{G}) \quad (B-46)$$

The G-vectors (and $\vec{k}$ later on) span the reciprocal lattice. In the following we suppress the parameter $\vec{q}$ as well as the vector symbols. $\phi(G)$ is supposed to be the screened version of the bare interaction coefficients ϕ_b , i.e.,

$$\phi(G) = \sum_{G'} \epsilon^{-1}(G, G') \phi_b(G') \quad (B-47)$$

where ϵ is the total dielectric function $\epsilon = \epsilon(q, G, G', \omega)$.

Without free carriers $\epsilon = \epsilon_v$, the valence-electron dielectric function, and the ordinary "unscreened" scattering potential is given by

$$\phi_o(G) = \sum_{G'} \epsilon_v^{-1}(G, G') \phi_b(G') \quad (B-48)$$

With free carriers present

$$\epsilon(G, G') = \epsilon_v(G, G') + \chi_c(G, G') \quad (B-49)$$

and the (longitudinal) free-carrier susceptibility χ_c is (Adler 1962)

$$\chi_c(G, G') = - \frac{e^2}{V |\vec{q} + \vec{G}|^2} \sum_{\lambda \lambda' k} \frac{f_{\lambda, k} - f_{\lambda', k+q}}{\hbar\omega + E_{\lambda, k} - E_{\lambda', k+q}} \eta_{G'}^* \eta_G \quad (B-50)$$

with

$$\begin{aligned} \eta_G &= \eta_G(\lambda', \vec{k} + \vec{q}; \lambda, \vec{k}) \\ &= \langle \lambda', \vec{k} + \vec{q} | \exp \left[i (\vec{q} + \vec{G}) \cdot \vec{r} \right] | \lambda, \vec{k} \rangle \end{aligned} \quad (B-51)$$

and the other symbols have their usual meaning.

For long wavelengths $q \ll G$, and consequently $G \neq 0$ terms in χ_c are relatively small so that we can make the approximation

$$\chi_c(G, G') \approx \delta_{G,0} \chi_c(0, G') \quad (B-52)$$

For insertion in (B-47) we now invert the total dielectric function (B-49) using the property (B-52).

$$\epsilon(G, G') = \sum_K (\delta_{G,K} + \sum_{K'} \delta_{G,0} \chi_c(0, K') \epsilon_v^{-1}(K', K)) \epsilon_v(K, G') \quad (B-53)$$

The inversion is most easily performed by considering the (G, G') as indices in a matrix. The result is

$$\begin{aligned}\epsilon_v^{-1}(G, G') &= \sum_K \epsilon_v^{-1}(G, K) \left[\delta_{K, G'} - \epsilon_c^{-1} \sum_{K'} \delta_{K, 0} \chi_c(0, K') \epsilon_v^{-1}(K', G') \right] \\ &= \epsilon_v^{-1}(G, G') - \epsilon_c^{-1} \epsilon_v^{-1}(G, 0) \sum_{K'} \chi_c(0, K') \epsilon_v^{-1}(K', G')\end{aligned}\quad (B-54)$$

where

$$\epsilon_c = 1 + \sum_K \chi_c(0, K) \epsilon_v^{-1}(K, 0) \quad (B-55)$$

and due consideration has been given to the terms neglected in (B-52) (Boguslawski and Mycielski 1977).

For the screened potential (B-47) we then find

$$\phi(G) = \phi_0(G) - \epsilon_c^{-1} \epsilon_v^{-1}(G, 0) \sum_K \chi_c(0, K) \phi_0(K) \quad (B-56)$$

Finally, we use a property of ϵ_v^{-1} in the long-wavelength limit $q \ll G$:

$$\epsilon_v^{-1}(G, 0) \approx \epsilon_\infty^{-1} \delta_{G, 0} \quad (B-57)$$

(Pick et al. 1970) where ϵ_∞ is the high-frequency dielectric constant of the material with no free carriers. Insertion in (B-55) and (B-56) yields

$$\phi(G) = \phi_0(G) - \delta_{G, 0} \sum_{G'} \frac{\chi_c(0, G')}{\epsilon_\infty + \chi_c(0, 0)} \phi_0(G') \quad (B-58)$$

This result is independent of band-structure complexity. It shows that the contribution to the potential due to free-carrier screening is isotropic since $G = 0$. This term has no interband matrix elements for $q = 0$ because the relevant wave functions are orthogonal. The optic deformation potential for $q = 0$ is consequently unaffected by free carriers as far as phonon renormalisation is concerned since no intraband contribution is counted for $q = 0$ (Chapter 4). Expressed in a different way, deformation potentials of Γ'_{25} (or Γ'_{12}) symmetry (only terms with $G \neq 0$) may well be screened by free carriers, but the screening contribution has Γ_1 symmetry ($G=0$).

This conclusion was not reached by Boguslawski and Mycielski (1977) because they considered carriers in a simple band minimum only. In that case only Γ_1 -type potentials are "picked up" in the matrix elements.

Lipnik (1969) considered a similar problem in a complex band structure, and from his results one may arrive at the same conclusion. However, his result is badly documented and treats the background dielectric function as nonlocal ($G=G'=0$) because the arguments are probably macroscopic. Moreover, his theory is constructed for acoustic deformation potentials only and is applied to ultrasonic phenomena where the frequency is too low for the theory to be reliable.

In our ultrasonic phenomena (Chapter 3), i.e., changes in elastic constants due to large free-hole concentrations, we have contributions from intraband matrix elements, but there screening is irrelevant because the holes have time to relax. The band structure of a statically strained crystal is not affected by free carriers.

The above treatment has avoided any detailed form of the free-carrier susceptibility $\chi_c(0,G)$, in particular that of holes. It is about time that this hole property was investigated further. Some work related to zero-gap materials has appeared, but it contains many simplifications and incorrect details.

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SUMMARY IN ENGLISH

The interaction between holes and phonons has been investigated by analysis of various shifts and broadenings of phonon and hole resonances. The analysis takes into account the complications of the hole dispersion relations and their influence on the interaction matrix elements (Appendices A and B).

Chapter 2 includes a summary of important prerequisites: The hole band-structure details, the definition of the deformation-potential constants b and d for acoustic as well as d_0 for optic-phonon interaction, and some qualitative consequences of the heavy acceptor doping needed for the production of large hole concentrations.

In Chapter 3, the influence of holes on ultrasonic resonances is studied, and the induced changes in the elastic constants are related to the acoustic deformation potentials. The theoretical treatment shows that a two-band model for holes is always inadequate. A subsequent numerical computation of the complete band-model results in satisfactory agreement between deformation potentials derived by the present method and previously determined values.

As a side-line, the influence of bound holes on the elastic constants is analysed, and some extraordinary effects occurring at low temperatures are interpreted by a model involving compensation. A ferroelastic instability is predicted, but can probably not be realised due to the presence of intrinsic strain fluctuations.

The hole-induced shifts and broadenings in the Raman spectrum are investigated in Chapter 4. The interference of the optic-phonon peak with a background due to direct intervalence-band transitions leads to nonsymmetric resonances (Fano effect), and existing experimental data have been reanalysed in terms of an improved model including the intrinsic shift and broadening of the optic phonon. The resulting extrinsic Lorentzian shifts and broadenings are related

to the optic-phonon self-energy calculated numerically, and the optic deformation potential d_o is found to be 27 eV in Si. For Ge, the situation is more complicated because impurity-induced distortions of the band structure play a significant role. The experimental results are interpreted with reasonable success in a model where the phonon wave vector is smeared over a typical reciprocal Bohr radius of the acceptors. The model involves a calculation of the wave-vector dependent self-energy, and an interesting structure in this variation has appeared. The overall result is $d_o = 27$ eV for Ge as well.

Chapter 5 deals with the influence of phonons on the hole energy spectrum, i.e. the inverse problem. An important qualitative result is that the effects due to the electron-phonon interaction do not follow $k \cdot p$ theory. This is well known for the polaron problem, but is here shown for the first time for the nonpolar interaction. Quantitatively, the broadening of the $(E_o + \Delta_o)$ structure in the interband spectrum is shown to be connected with the limited lifetime of the spin-orbit split-off hole at $k=0$ due to optic-phonon emission, and the optic deformation potential d_o is determined for a number of semiconductors. For Ge, $d_o = 39$ eV is found in this way, and the difference between this value and that previously derived is explained in terms of a direct spin-orbit contribution to the deformation potential.

In addition to a general conclusion, Chapter 6 contains a preliminary discussion of possible extensions of the phonon shift and broadening method to intervalley phonons. A more detailed consideration of free-carrier screening is needed before useful results can be obtained in this way.

DANSK RESUME/SUMMARY IN DANISH

Vekselvirkningen mellem huller og fononer undersøges ved analyse af forskellige forskydninger og udbredninger i fonon- og hulresonanser. Analysen medtager alle komplikationer i huldispersionsrelationerne og deres betydning for vekselvirkningens matrixelementer (Appendices A og B).

Kapitel 2 omfatter et sammendrag af vigtige forudsætninger: Hulbåndstrukturdetaljerne, definitionen af deformationspotentialkonstanterne b og d for den akustiske såvel som d_0 for den optiske fononvekselvirkning samt nogle kvalitative følger af den kraftige akceptordotering, der er nødvendig for at frembringe virkeligt store hulkoncentrationer.

I kapitel 3 studeres hullers indflydelse på ultralydsresonanser, og de således inducerede ændringer i de elastiske konstanter sættes i relation til de akustiske deformationspotentialer. Den teoretiske behandling viser, at en to-bånds-model for huller altid er utilstrækkelig. En efterfølgende numerisk beregning med den komplette båndmodel fører til en tilfredsstillende overensstemmelse mellem deformationspotentialer d afledt ved denne metode og tidligere bestemte værdier.

Som et biprodukt undersøges bundne hullers indflydelse på de elastiske konstanter, og nogle usædvanlige effekter, der viser sig ved lave temperaturer, fortolkes på grundlag af en model med kompensation. Derved forudsiges en ferroelastisk instabilitet, men denne kan dog næppe realiseres på grund af intrinsiske deformationsfluktuationer.

De hulinducerede forskydninger og udbredninger i Ramanspektret behandles i kapitel 4. Interferensen mellem den optiske fononspids og den baggrund, der forårsages af direkte intervalensbåndovergange, fører til usymmetriske resonanser (Fanoeffekt), og de foreliggende eksperimentelle data er genanalyseret på grundlag af en forbedret model, der omfatter den optiske fonons intrinsiske forskydning og udbredning. De udledte ekstrinsiske forskydninger og udbredninger af Lorentztypen sammenlignes med den numerisk beregnede

fononrenormering, og det optiske deformationspotential d_0 findes derved til at være 27 eV i Si. I Ge er situationen mere indviklet, fordi de af urenhederne frembragte forvrængninger af båndstrukturen spiller en betydelig rolle. De eksperimentelle resultater kan fortolkes nogenlunde tilfredsstillende på basis af en model, i hvilken fononens bølgevektor er udsmyrt over en typisk reciprok akceptor-Bohrradius. Modellen omfatter en beregning af den bølgevektorafhængige renormering, og der viser sig en interessant struktur i denne variation. Slutresultatet er $d_0 = 27$ eV også i Ge.

Kapitel 5 omhandler fononernes indflydelse på hulenergispektret, altså det omvendte problem. Som et vigtigt kvalitativt resultat findes det, at virkningerne af elektron-fononvekselvirkningen ikke følger $k \cdot p$ teori. Dette er velkendt for polaronproblemet, men er her for første gang vist at gælde også for den ikke-polære vekselvirkning. Kvantitativt vises det, at udbredningen af $(E_0 + \Delta_0)$ strukturen i interbåndspektret er forbundet med den begrænsede levetid af det "spin-banefraspaltede" hul ved $k=0$ som følge af optisk fononemission, og det optiske deformationspotential d_0 bestemmes heraf for en række halvledere. For Ge findes derved $d_0 = 39$ eV, og forskellen mellem denne værdi og den tidligere afledte udlægges som et direkte spin-banebidrag til deformationspotentialet.

Ud over en almindelig konklusion indeholder kapitel 6 en foreløbig diskussion af mulige udvidelser af fononrenormeringsmetoden til intervalley fononer. Førend brugbare resultater kan fås på denne måde kræves der en mere dybtgående behandling af teorien for skærmning ved frie ladningsbærere.

